Synthesis and Characterization of Cu_2O/ITO Thin Film by Using Electro-deposition Method

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Abstract

Cuprous oxide (Cu_2O) thin film was deposited onto ITO coated glass substrates by the electrodeposition method. The crystallographic structure of the thin film was studied by X-ray diffraction (XRD). XRD measurement showed that the film was crystallized in the cubical phase. The grain size of the thin film was studied by scanning electron microscope (SEM). Optical properties were measured by using Shimadzu UV-1800 spectrophotometer. Optical properties such as refractive index (n), extinction coefficient (k) absorption coefficient (α), and energy band gap were calculated from absorption and transmission spectra by using envelope method.

Keywords: *Cu_2O, XRD, SEM, UV-Vis, Band gap*

INTRODUCTION

In recent years, the synthesis and characterization of semiconductor particles attracted great attention because of their usage in many areas such as solar cells, heat mirrors, gas sensors, wear-resistant applications, thin film resistors, dye-sensitized solar cells and in biological applications [Ali İmran Vaizoğullar & Ahmet Balcı, 2014]. One dimensional oxide semiconducting materials have attracted a lot of attention for potential application in optoelectronic devices due to their large surface area-to-volume ratio [Tsai T.Y. et al, 2011].

A semiconductor is a material that has an electrical conductivity between a conductor and an insulator. In semiconductors, the highest occupied energy band, the valence band is completely filled with electrons and the empty next one is the conduction band [Sagadevan Suresh, 2013,]. Semiconductor thin films are always important in materials science due to their outstanding electrical and optical properties, which are useful in various photoelectronic devices [S.Sivapriya & K.Balasubramanian, 2017]. A small selection of applications of thin films are eyeglasses, microelectronics, drill bits and cutting tools, solar cells, mirrors, flat screens and windows [Daniel Magnfält,2014].

Cuprous oxide (Cu_2O) is naturally a p-type direct bandgap semiconductor with cubic crystal structure and room-temperature band gap energy of 2.17 eV [Yuxi W., et al, 2014]. Cu_2O has the advantages of low consumption, nontoxic, and higher conversion efficiency. Therefore, it is widely used in solar cells, lithium ion batteries, biological sensors, gas sensors, magnetic storage, microdevices, and negative electrodes [Xishun J., et al, 2014]. Cu_2O thin films are prepared by various methods like reactive sputtering, vacuum evaporation, chemical

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and thermal oxidation and electrodeposition. Deposition of Cu_2O thin films by electro-deposition from aqueous solution is an inexpensive technique with low temperature [T. Mahalingam, et al, 2006].

Experimental Procedures of Cu_2O thin film

Cu_2O Sol-solution preparation

Firstly, 0.2 g of Copper (II) sulphate (Cu_2SO_4), 6 ml of Lactic acid ($C_3H_6O_3$) and 4 g of sodium hydroxide (NaOH) were mixed with 25 ml of deionized (DI) water, respectively. The three solutions were remixed and stirred by magnetic stirrer at 700 rpm for 1 hr, till the mixture solution became pH-10. Then, this solution was deposited onto ITO glass substrate by electrochemical deposition method.

Deposition Process

Firstly, ITO glass substrate was wet-cleaned with acetone and deionized water, and then baked at 80 ºC for 10 min to evacuate moisture. Cu_2O sol-solution was treated as bath temperature at 100 °C. The ITO glass substrate and copper plate were placed into plating solution and connected it to the cathode and anode of power supply. Parameter that affects the electroplating process was used to 5 volts in 1 hr. After depositing, the Cu_2O/ITO thin film was annealed in air at 150 °C for 30 min. The crystalline quality and phase content of thin film were analyzed by X-ray diffractometer (XRD). The surface morphology of thin film was observed by using Scanning Electron Microscope (SEM) JEOL - JSM 5610 LV. Optical absorbance and transmittance measurements were measured by using Shimadzu UV-1800 spectrophotometer.

RESULTS AND DISCUSSION

XRD analysis of Cu_2O/ITO thin film

The crystal structure and phase formation of Cu_2O/ITO thin film was examined by using X-ray diffraction. Figure (1) showed the XRD patterns of Cu_2O/ITO thin film. The upper side of XRD profile was represented the observed profile while the lower side showed the standard JCPDS (Joint Committee on Powder Diffraction Standards). Form XRD plot, the Bragg reflections at 2θ were 36.408°, 42.285° and 61.289° that could be indexed to the (111), (200) and (220), prominent orientations, respectively, and confirmed the presence of Cu_2O in the XRD pattern. XRD measurement showed that the film was crystallized in the cubical phase. The average lattice parameter of the thin film was found to be 4.2711 Å in a-axis. The diameter of cubical shaped crystallite could be identified as crystallite size, which was calculated by Debye-Scherer equation;

$$G = \frac{k \times \lambda}{B \times \cos \theta_B} \qquad (1)$$

where G and is the crystallite size, k is a constant equal to 0.9, λ is the wavelength of the X-ray, θ is the diffraction angle and B is the full width at half maximum (FWHM) of the diffraction peak. The average crystallite size was found to be 0.249 nm in Table (1).

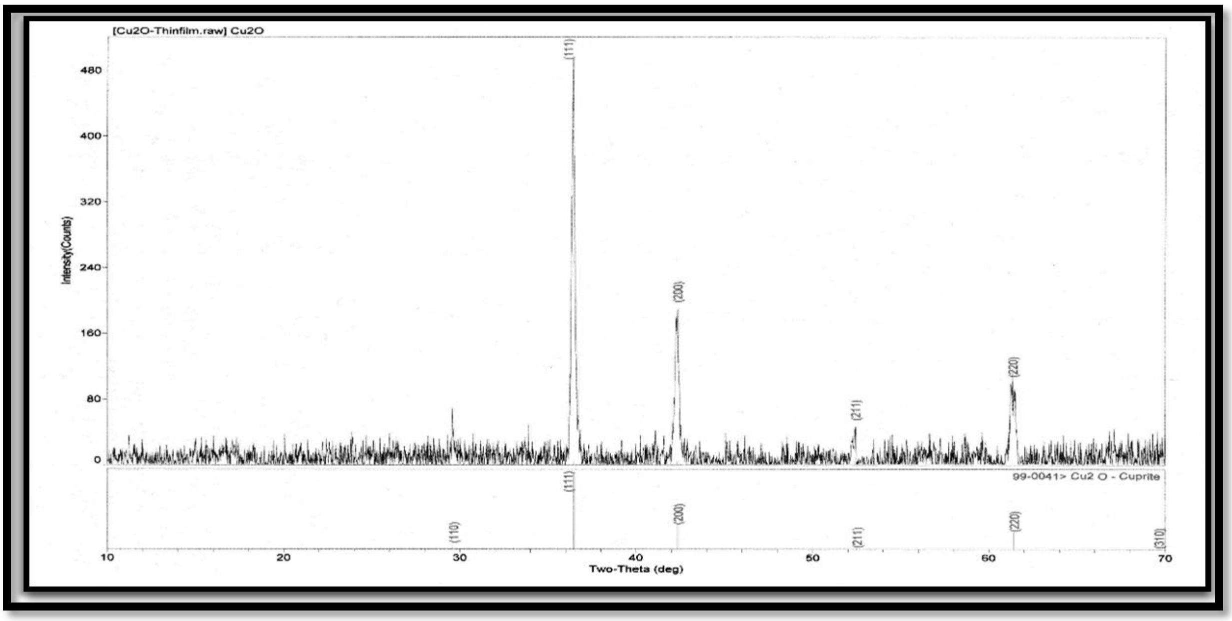

Figure (1) XRD pattern of Cu_2O/ITO thin film

Table (1) Crystallite size of Cu_2O/ITO thin film

No	Peaks	FWHM (deg)	Crystallite size (nm)
1	(110)	0.048	0.017
2	(111)	0.148	0.591
3	(200)	0.158	0.530
4	(211)	0.074	0.018
5	(220)	0.268	0.341
Average crystallite size			0.249

SEM Analysis of Cu_2O/ITO thin Film

SEM microphotograph of Cu_2O thin film at process temperature of 150°C for 1 hr was shown in Figure (2). The grain distribution was not uniform in this image. Almost of the grains were in continuity. The shape of grain was cubical feature and the grain size was measured to be 0.494 μm.

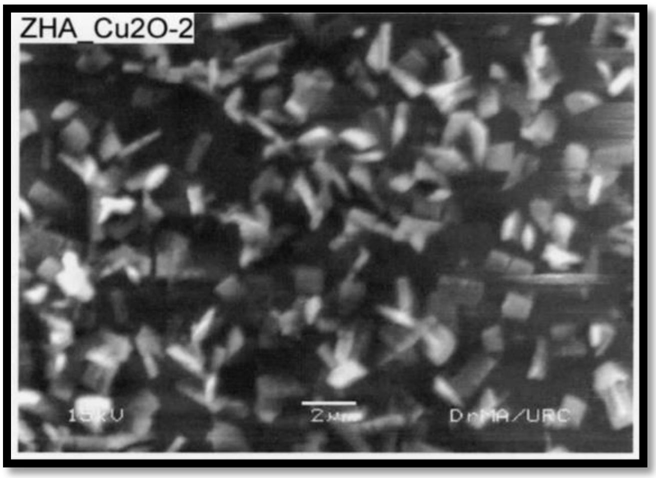

Figure (2) SEM image of Cu_2O/ITO thin film

UV-Vis Analysis of Cu_2O/ITO thin film

Optical absorption studies are important to determine the optical band gap of semiconductor films, and for understanding the optoelectronic properties of the growing semiconductor. The absorbant spectra in the visible region of the deposited Cu_2O/ITO thin film synthetized at deposition time are displayed in Figure (3). The optical measurements were carried out at room temperature by using a Shimadzu UV-1800 spectrophotometer in the wavelength range from 250.00 nm to 900.00 nm. The absorption peaks were 286.00 nm and 579.00 nm. The cut off wavelength of absorption spectrum was 533.3 nm. The optical energy band gap was calculated by Planck's Method;

$$E_g = \frac{hc}{\lambda} \qquad (2)$$

where E_g, h, c and λ are the energy band gap (eV), Planck's constant (6.625×10^{-34} J-s), the speed of light (3×10^{8} ms^{-1}) and wavelength (nm), respectively. The calculated optical band gap from absorption spectrum was 2.31eV.

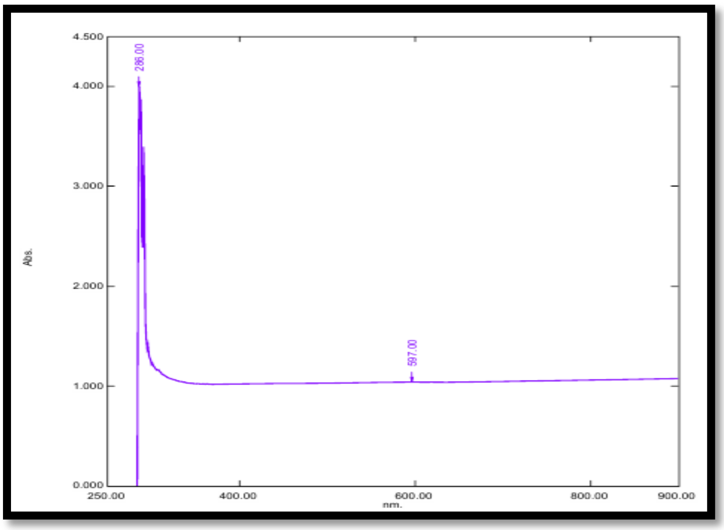

Figure (3) Absorption spectrum of Cu_2O thin film

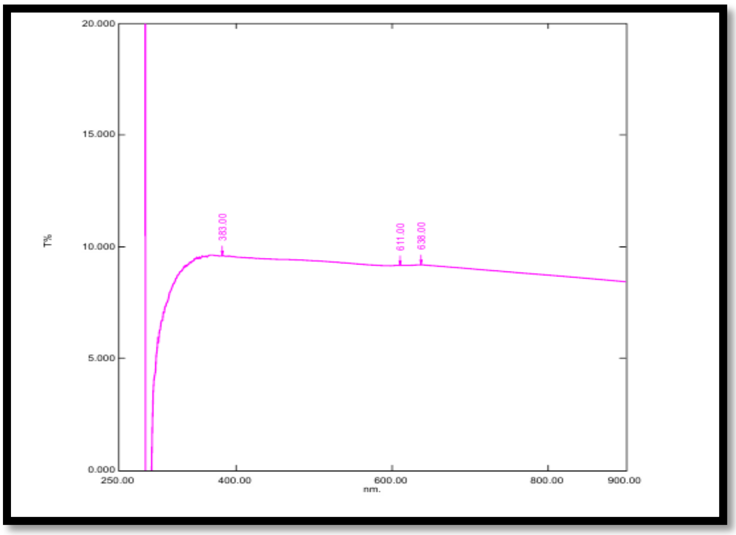

Figure (4) Transmission spectrum of Cu_2O thin film

The widely used envelope method has been developed for transmittance measurements to evaluate the refractive index, extinction coefficient and absorption coefficient. The optical band gap (E_g) and absorption coefficient (α) could be evaluated from transmittance or absorbance spectra [Manifacier.J et al, 1976, V.V. Brus et al, 2011].

An excellent surface quality and homogeneity of the film were confirmed from the appearance of interference fringes in the transmission spectrum occurring when the surface of film is reflecting without much scattering/absorption in the bulk of the film. The optical constants were evaluated by using the envelope method originally developed by Manifacier et al. Swanpoel's envelope method was employed to evaluate the optical constants such as the refractive index (n), extinction coefficient (k), and absorption coefficient (α) from the transmittance spectrum [M.Caglar et al, 2006, Swanepoel.R, 1983]. Figure (4) revealed transmission spectrum of Cu_2O thin film. The transmission peaks were 385.00 nm, 611.00 nm and 638.00 nm.

The thickness of the film was calculated by using the following relation;

$$t = \frac{\lambda_1 \lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \qquad (3)$$

where n (λ_1) and n (λ_2) are the refractive indices at the two adjacent maxima (or minima) at λ_1 and λ_2. Cu_2O thin film thickness was calculated to be 0.187 µm by using equation (3).

The optical constants such as refractive index (n) and extinction coefficient (k) were determined from a transmittance spectrum by using envelope method. The refractive index can be calculated from the following equations:

$$n = [N + (N^2 - n_s^{\ 2})^{\frac{1}{2}}]^{\frac{1}{2}} \qquad (4)$$

$$N = \frac{(n_s^2 + 1)}{2} + 2n_s \frac{(T_{max} - T_{min})}{T_{max} T_{min}} \qquad (5)$$

where n_s is the refractive index of the substrate. T_{max} and T_{min} are maximum and minimum transmittances at the same wavelength in the fitted envelope curves on the transmittance spectrum. The extinction coefficient can also be calculated by the following equation [Seniye.K et al, 2015]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

The variation of refractive index (n) as the function of wavelength for thin film was shown in Figure (5). The refractive index of the thin films exponentially decreased with the wavelength. The extinction coefficient (k) of the thin films proportionally increased with wavelengths as shown in Figure (6). The absorption coefficient (α) of thin film was determined from transmittance measurement. Since the envelope method is not valid in the strong absorption region, the calculation of the absorption coefficient of the film in this region was performed by using the following expression;

$$\alpha(\nu) = -\frac{1}{t}\ln(T) \quad (7)$$

where T is the normalized transmittance and t is the film thickness [Gumus C., et al, 2006]. These absorption coefficients were used to determine the optical energy gap. Figure (7) showed the plot of $(\alpha h\nu)^2$ versus hν for the thin film, where α is the optical absorption coefficient and hν is the energy of incident photon. The energy gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression [Reddy.P.S et al, 1991 and Vijay.B.S et al, 2011]:

$$\alpha h\nu = K\,(h\nu - E_g)^{1/2} \quad (8)$$

Where K is a constant, the band gap (E_g) was determined from each film by plotting $(\alpha h\nu)^2$ versus hν and then extrapolating the straight line portion to the energy axis at $(\alpha h\nu)^2 = 0$. The band gap energy E_g was obtained for each thin film. From this drawing, the optical energy band gap was deduced to 2.34 eV for Cu_2O thin film. Table (2) showed the optical band gap of Cu_2O thin film by using absorption spectrum and Transmission spectrum.

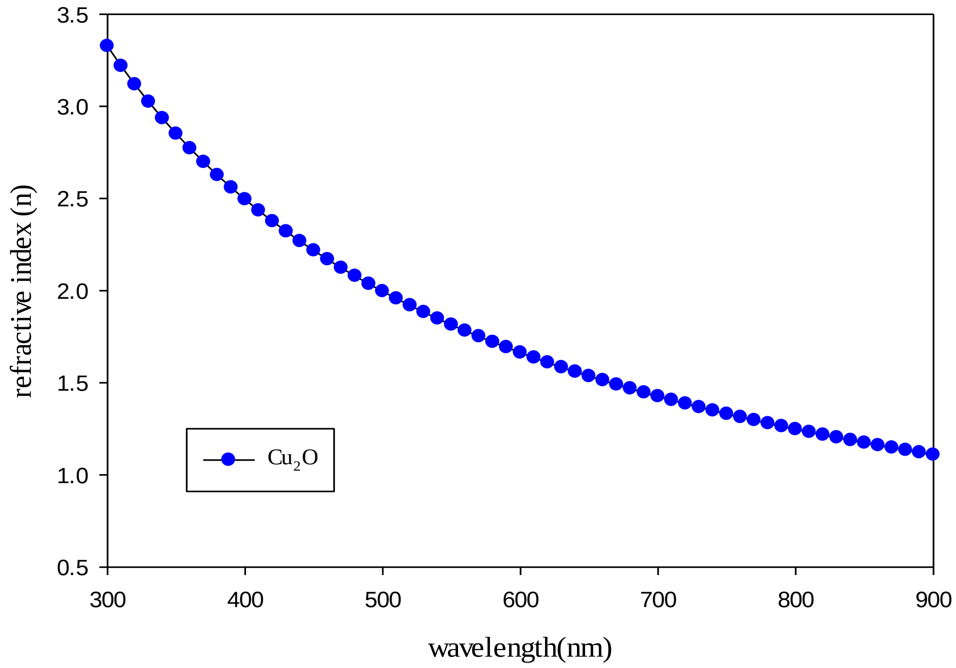

Figure (5) Plot of refractive index (n) as a function of wavelength of Cu_2O thin film

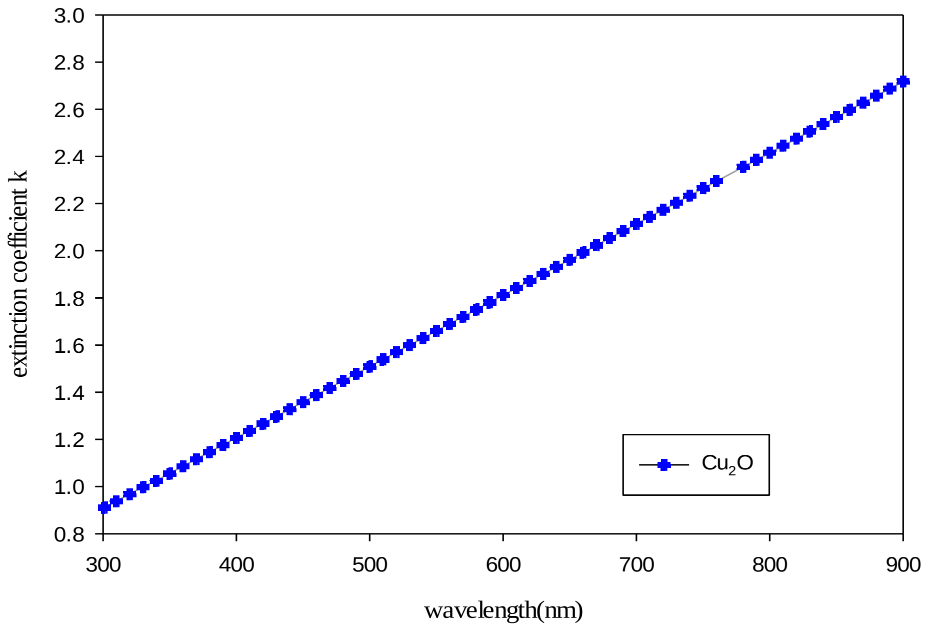

Figure (6) Plot of extinction coefficient (k) as a function of wavelength of Cu_2O thin film

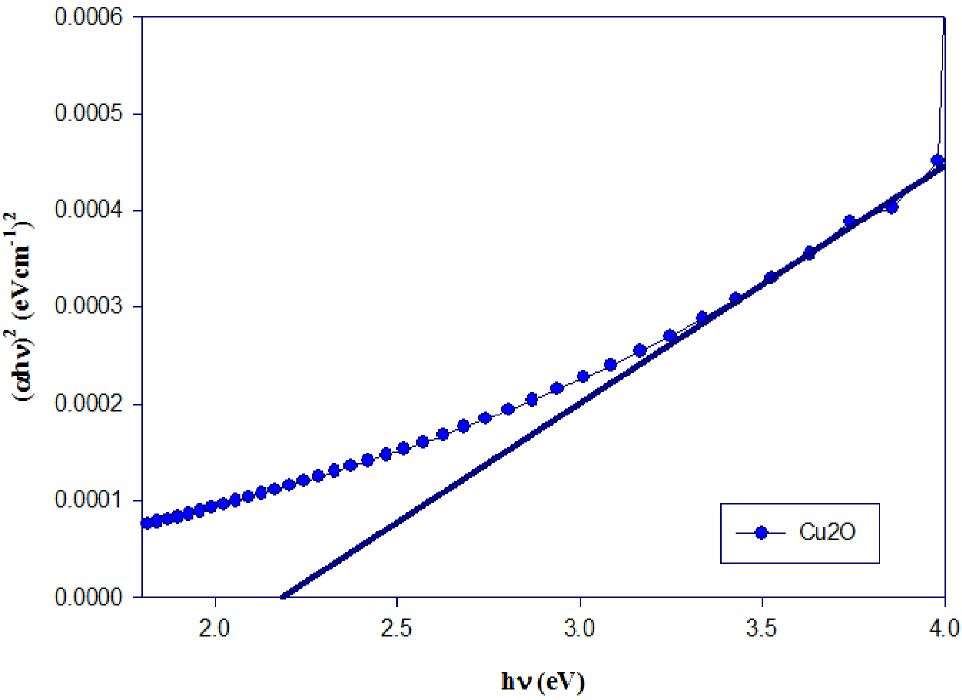

Figure (7) Plot of $(\alpha h\nu)^2$ versus hν for Cu_2O thin film

Table (2) Optical band gap of for Cu_2O thin film by using absorption spectrum and transmission spectrum

Cu_2O	Absorption spectrum	Transmission spectrum
E_g	2.31 eV	2.21 eV

CONCLUSION

Cuprous oxide (Cu_2O) thin film was deposited onto ITO coated glass substrate by the electrodeposition method. XRD analysis showed that the Cu_2O/ITO film is crystallized in the cubical phase. The average crystallite size was observed to be 0.249 nm. Scanning election microscope (SEM) analysis showed that the grain size was estimated to be 0.494 µm. UV-Vis absorption and transmission spectra of Cu_2O thin film were measured by Shimadzu UV-1800 spectrophotometer. The refractive index of the thin films exponentially decreased with respect to the values of wavelength. The extinction coefficient (k) of thin films proportionally increased with wavelengths. Cu_2O thin film thickness was calculated to be 0.187 µm by using enevolpe method. The film had a direct band gap with an optical value of 2.31eV from absorption spectrum and 2.21eV from transmission spectrum, which were closed to the value of bulk material of 2.17eV.

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