Synthesis of copper oxide thin films by electrolysis method based on Porous Silicon for Solar Cell Applications

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Abstract. Copper oxide thin film was successfully prepared by electrolysis method and deposited on glass and porous silicon substrates. The main goal of this paper is to study the properties of copper oxide thin films and prepare a solar cell of low cost and good efficiency. These properties were optimized at annealing temperature (200) °C. The transmission spectrum were studied for the prepared thin film showed good transparency in the visible region.  The structure of films was characterized by X-ray diffraction. The average grain size of the thin film from AFM analysis is about 46.3 nm. The energy bandgap is found to be (3.8) eV this wide bandgap is due to the quantum size effect. The solar cell efficiency is found to be (12.9%).

Keywords: copper oxide, thin film, solar cell, electrolysis

1. Introduction

Solar cells are future energy resources. Silicon is a conventional semiconductor material used for solar cells. The reduction in the cost of solar cells is the most important issues. [1]. Copper has two major oxide phases, Cu$_2$O and CuO. Both are p-type semiconductors. The energy bandgap for bulk Cu$_2$O is 1.8–2.5 eV and for bulk, CuO is 1.2–1.9 eV. They are promising semiconductors for solar cell applications due to their electrical and optical properties, as well as nontoxicity, natural abundance and inexpensive [2]. Thin films Copper Oxide have been prepared using various techniques such as sputtering process, chemical vapour deposition, electro-deposition, vacuum evaporation, thermal oxidation, chemical solution deposition, electron-beam Evaporation [3–6].

In this work, we discuss the effect of annealing on the properties of copper oxide thin film, photovoltaic properties and its applications in the solar cell this thin film were prepared by electrolysis method. The film was characterized using UV-Vis spectrophotometer, (AFM), (XRD) and I-V characteristics at dark and illumination conditions.
2. Experimental:

The steps for preparing copper oxide thin film and porous silicon were summarized in this section.

2.1. Preparation of substrates

In this work, 2 x 2 cm$^2$ and glass n-type silicon (1-10) Ω·cm, (2×1.5) cm dimensions substrates were used with a thickness of 0.1 cm. The substrates were cleaned using methanol and deionized water in the ultrasonic bath in order to get a clean surface contact for the next process.

2.2. Preparation of copper oxide solution using the electrolysis method

Copper nanoparticles have been prepared by electrolysis cell. The electrodes are copper as a positive electrode and gold as a negative electrode. Water was used with Hydrochloride (HCl) in ratio about 8:1 as an electrolyte liquid. The applied voltage is (6) Volt.

2.3. Preparation of porous silicon substrate

The porous Silicon (PS) layers were fabricated by anodic etching with an electrochemical cell where 0.785 cm$^2$ etched area substrate was placed in the Teflon etching cell using an admixture of 1:1 ethanol (purity 99.99%) and aqueous hydrogen fluoride (50% purity). The sample was anodized at a current density of (15) mA/cm$^2$ for (15) min etching time. No further thermal or chemical treatment was carried after etching.

![AFM images of the porous silicon (PS)](image)

**Figure 1.** AFM images of the porous silicon (PS)

2.4. Preparation of copper oxide thin films deposition by Drop-casting method

The drop-casting method has been used to deposit a Cu nanoparticles solution on glass and PS samples. The annealing process at (200) °C is then applied for (90) minutes to the samples to get the copper oxide. Thin film thickness is found to be (200±10) nm the thickness of the film is measured using (Fizeau Interferometer Method). The bottom of the (PS) sample is coated with thick aluminium of very high purity (99.99%) in a vacuum. At a pressure of (5x10$^{-6}$) mbar. In addition, silver paste was added on the top layer of the copper oxide to measure the electrical properties.

2.5. Samples Characterization

The crystal structure was studied at the following operation conditions- Source Cu-Kα radiation of wavelength (λ=1.5405 Å), Voltage =4 kV, Current =20 mA, Scanning speed = 5 cm/min by XRD 6100 Shimadzu. Optical transmittance measurements were complete with (UV/Visible 1800 spectrophotometer). The energy bandgap of the thin film was specified from the optical transmittance.
spectrum (300-1100nm). The shape and size of copper oxide were investigated by using XRD and AFM (AA 3000 Scanning Probe Microscope).

3. Results and Discussion

The obtained results from the experiment are discussed in this section.

3.1. Structural properties of copper oxide thin films

Fig. 2 shows the diffraction pattern of copper oxide film deposited on glass substrates annealed at (200) ºC. Analysis of diffraction spectra indicates two peaks positions for Cu$_4$O$_3$ at crystal planes, 47.47°, 57.74°. In addition, there are two peaks of CuO$_2$ at crystal planes, 28.97°, and 39.93°. CuO$_2$ is not stable and it will decay to one of the stable forms of copper oxide. Also, the figure shows two peaks of Cu$_2$O at crystal plane, 27.91° and 42.16° and one peak of (Au$_2$O$_3$) at a crystal plane, 27.91°. These peaks were associated with the reflection of the peaks of (COD) cards no. (96-210-5391, 96-152-1321, 96-900-7498, 96-900-5770 and 96-900-0604) [7]. The (Au$_2$O$_3$) peak is present as a result of using a gold electrode in the electrolysis cell. When saturation state accrues a reverse current may flow and this will lead to getting Au nanoparticles. Au$_2$O$_3$ is a narrow bandgap semiconductor (0.83) eV [8]. According to the pattern, results have a small peak and the film shows a good crystallinity.

![Figure 2. XRD pattern for copper oxide thin film annealed at 200 °C.](image)

The grain size was calculated using Debye-Scherrer’s equation [9]:

$$G_s = \frac{0.94\lambda}{B\cos\theta}$$

(1)

Where ($\lambda$) represents the wavelength of X-ray radiation, ($G_s$) represents the grain size, (θ) is the angle of diffraction and (β) is the full width at half maximum.

The value of dislocations density ($\delta$) and strain value ($\varepsilon$) can be calculated by using the next relations [10]:

$$\delta = \frac{1}{(G_s)^2}$$

(2)

$$\varepsilon = \frac{\beta \cos \theta}{4}$$

(3)
Fig. 3 shows a (3-D) AFM image of the thin film. AFM image explains that the grains are distributed uniformly within the scanning area (1600×1600nm) with individual straight grains growing upwards. The average grain size is calculated from AFM analysis using the software is found to be (46.3) nm.

**Figure 3.** AFM images of copper oxide thin film annealed at 200 °C

### 3.2. Optical properties of copper oxide thin films

The transmittance as a function of wavelength is shown in Fig. 4. It is found that the transmittance of the film increase with the increasing of the wavelength. At UV-region, the transmittance is sharply decreased as a result of the wide of absorbed particle size.

**Figure 4.** Transmission spectra for copper oxide thin film annealed at 200 °C

Fig. 5 shows the energy bandgap of copper oxide measured from the plotting $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ where $(\alpha$ is the coefficient of absorption). By taking, a straight line from the linear section of the curve toward the x-axis, which represents the photon energy. $(E_g)$ is found to be 3.8 eV, this results in good agreement with [11]–[14]. The wide bandgap is due to the quantum size effect.
Figure 5. \((ahv)^2\) versus \(E_g\) of copper oxide thin film annealed at 200 °C

3.3. Electrical properties of the heterojunction

Fig. 6a and Fig. 6b Shows the I-V characteristics at the dark condition and in the presence of light respectively which confirm the heterojunction behaviour of (p-copper oxide/n-PS) junction and Fig. 7 Shows The measurement of the open-circuit voltage, short-circuit current, fill factor and the efficiency all data are explained in Fig 7 under (40 μwatt) light power. This figure represents the I-V curve at the light condition with the existence of variable resistance. This experiment is a simple method to measure the efficiency of a solar cell. There are two factors we need to find, short-circuit current (Isc) occurs when \(R = 0\) so that \(V = 0\) and The second factor is the open-circuit voltage (Voc) occurs when \(R \rightarrow \infty\), in this case, the net current is zero. From these two points, we can find the maximum power rectangle and calculate the efficiency of the solar cell using equation (4). All results of the heterojunction p-copper oxide/n-PS confirm that this heterojunction could be used in solar cell applications [15].

Figure 6. a) the I-V characteristics in the dark condition of the (p-copper oxide/n-PS) heterojunction annealed at 200 °C

The solar cells conversion efficiency depends on the morphology of interfaces.

\[
\eta = \frac{V_{ml}J_{m}A_2}{P_{in}A_1} \times 100 \% \tag{4}
\]
$(\eta)$ is the efficiency of the solar cell, $(V_m)$ is the maximum output voltage, $(I_m)$ is the maximum output current, $(P_m)$ is the light source power which is equal to (40) $\mu$watt in our experiment. $(A_1)$ is the area of the solar cell sample of radius $(0.5)$ cm. $(A_2)$ is the area of the electric contacts which have a value of $(0.04)$ cm$^2$.

![Figure 6](image)

**Figure 6.** b) the I-V characteristics in the light condition of the (p-copper oxide/n-PS) heterojunction annealed at $200 \, ^\circ$C

![Figure 7](image)

**Figure 7.** open-circuit voltage of the (p-copper oxide/n-PS) heterojunction annealed at $200 \, ^\circ$C

4. Conclusion

In the present work, copper oxide thin films prepared by electrolysis method for solar cell applications has been studied. The prepared thin film shows good transparency in the spectral range (350-1100) nm the energy bandgap is found to be (3.8 eV). This wide bandgap due to the quantum size effect. The performance of the solar cell heterojunction has been improved by the porosity of Silicon and the existence of the gold oxide that form sublevels inside the bandgap of copper oxide that helps to increase the charge carriers that share in the conduction process. The solar cell efficiency is (12.9%).
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