Effect of Annealing on Copper Oxide Thin Films and Its Application in Solar Cells

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Abstract. Cupric Oxide (CuO) thin films were prepared by chemical spray pyrolysis (CSP) method at 400°C on glass and p-type Si substrate and then the films were annealed at 500°C and 600°C. The structural, optical and electrical properties of the thin films are measured. The analysis of X-ray diffraction (XRD) has confirmed amorphous phase mixed with polycrystalline features in the form of monoclinic structure. However, the polycrystalline CuO disappeared and changed to crystallite phase with increasing of annealing temperature. The values of bandgap energy (Eg) of the films were calculated using the absorbance data recorded by a spectrophotometer (UV-VIS). The calculated Eg using Tauc plot was about 2.45 eV which increased with increasing of annealing temperature. CuO thin films with high conductivity have been used to fabricate a heterojunction solar cell of CuO/p-Si at 600°C which gives Rs= 111Ω, Rsh = 7kΩ and a conversion efficiency of 1.24×10^{-4} %.

1. Introduction
Copper oxides (CuO) are one of the most important materials that have a high absorption coefficient (10^4 cm^{-1}). CuO films have been already prepared using different methods like electro deposition method [1], sputtering [2], and spin-coating [3]. Availability of CuO in nature, and being non-toxic material made it an important material in electronic and optoelectronic applications [4]. CuO is a well-known p-type semiconductor [5, 6]. However, many attempts have been implemented to convert it from p-type to n-type by doping [7], annealing [8].

It is well-known that the temperatures of the heat treatment of all materials increases the crystallinity and produce a specific microstructure, thus a marked effect on the properties of the materials [9]. Many researchers have shown that increasing the temperature of the preparation or heat treatment after the preparation process above 400°C can convert the material conductivity from p to n-type [10, 11]. Also, it was reported that the conversion is coming from oxygen vacancies introduced at high temperatures.

Researchers reported the deposition of CuO thin films on p-type Si substrates, and studied their characteristics [12, 13]. However, few numbers have used CuO/Si junctions as solar cells. In this work, we introduce a simple approach to fabricate CuO/Si heterojunction solar cell using spray pyrolysis methods.

2. Experimental
CuO thin films were deposited on p-Si wafers resistivity 10Ω.cm and ordination < 110> and glass substrates by spray pyrolysis method. Cu (NO3)2.3H2O solution molarity 0.1M dissolved in distilled water. The solution has been sprayed in Diagonal angle 45°, with 3 sec step 30 sec spraying time total. The films were annealed at 500°C and 600°C for 2 hour. The structure of the CuO films was investigated by X-ray diffraction (XRD - 6000 / Shimadzu). The target is Cu with wavelength λ=0.15418 nm which is for Kα-line. The film thickness was informed from FESEM images (cross-section imaging) using Tescan Mira3/ France.

The energy band gap and absorption coefficient were calculated from the data collected by (Shimadzu UV-Visible Spectrometer UV-1650PC) with wavelength range (400-1100nm). The measurements of Hall Effect were implemented on 9×9 mm2 CuO thin films with applied magnetic field 0.25 Tesla. The resistivity of the films was determined using a homemade four point probe.
3. Results and discussion

3.1. Structural properties

The data of XRD for CuO thin films are presented in Figure 1. The diffraction patterns reveal that cupric oxide thin films prepared by CSP exhibit amorphous features with some polycrystalline nature. The crystalline phases have monoclinic structure with preferential orientation (002) and (111). The data are well-matched with the standard ASTM cards for monoclinic CuO. With increasing of annealing temperature, the peaks become sharper and more intense revealing enhanced crystallite size. The fingerprint peaks appear at 2θ(hkl) = 35.6º(002) and 38.8º(111).

![Figure 1. XRD data for as-deposited CuO at substrate temperature 400 ºC and after annealing at 500ºC, 600ºC for 2 hours.](image)

The annealing process leads to increase the peak intensity and crystallite size. Depending on these results, the parameters like the crystallite size (D) and the dislocation density (δ) of the films have been obtained from Scherrer’s relation [14].

\[
D = \frac{0.94\lambda}{\beta\cos\theta}
\]

\[
\delta = \frac{1}{D^2}
\]

where β which is equivalent to the full-width at half maximum (FWHM) of the peaks should be in radian. λ is the wavelength of x-ray radiation and θ is Bragg’s angle. The increasing of annealing temperature results in an arrangement of crystal structure and hence reduced dislocation density. This result agrees well with [15, 12].

Significant topographic changes with increased annealing temperature have been informed from the FESEM images. The annealing process obviously leading to enhanced growth of the CuO crystals in the films as indicated in Table (1). These results are compatible with [16].
Figure 2. FESEM image for CuO thin film after annealing process. Annealing temperature are: (A) deposited at 400ºC (B) and (C) annealed at 500ºC and 600ºC respectively.
3.2. Optical properties
The energy bandgaps are calculated from the extrapolation of the straight part to intercept the x-axis (hν). In hν-(αhν)² plot, according Figure 3. The band gap energy values for CuO thin films, deposited at 400°C and after annealing at 500°C and 600°C for 2 hours, are found to increase from 2.45, 2.55, and 2.6 eV respectively. This behavior is compatible with that of Kavit [16].
Figure 3. Plot of $(\alpha h \nu)^2$ vs $h \nu$ for cupric oxide thin films at various annealing temperatures.
The Urbach energy $E_u$ is decreasing with the increasing of band gap energy. The calculated $E_u$ values are (1.04, 0.88 and 0.78 eV) as shown in Table (1). This is because that increasing of annealing temperature reduces the number of defects and the dislocation density. Table (1) summarizes the calculated optical parameters.

![Figure 4. Urbach Energy of cupric oxide thin films deposited at substrate temperature 400ºC and for sample after annealing at 500ºC and 600ºC.](image)

**Table 1.** Sample parameters for cupric oxide thin films deposited by spray pyrolysis at various annealing temperatures.

| $T(ºC)$ | $D$ (nm) | $\delta$ (nm)$^2$ | $E_g$ (eV) | $E_u$ (eV) |
|---------|----------|--------------------|-------------|------------|
| $C_1$   | 400      | 4.8 $\times 10^{-3}$ | 2.45        | 1.04       |
| $C_A1$  | 500      | 9.7 $\times 10^{-2}$ | 2.55        | 0.88       |
| $C_A2$  | 600      | 19.5 $\times 10^{-3}$ | 2.6         | 0.78       |

The absorption coefficients ($\alpha$) increases with increasing of annealing temperature for CuO thin films. The absorption coefficient values for $\lambda=633$nm are (2$\times10^4$, 6$\times10^4$ and 7$\times10^4$ cm$^{-1}$). For as-deposited CuO at 400ºC and annealed samples at (500ºC and 600ºC), these results have good agreement with other researchers [17, 18]. It was reported that the enhancement in absorption coefficient is due to improved arrangement of the atoms and reduced number of defects and hence lower Urbach Energy values.

### 3.3. Electrical properties

Hall effect measurements are implemented to identify type and concentration of charge carriers in the copper oxide. The values of conductivity ($\sigma$) and mobility ($\mu_H$) is inserted in Table (2). It is found that the concentration of carriers increase with increasing of annealing temperature and the type of samples CuO is p-type. The enhancement in conductivity of CuO thin films is due to improved number of oxygen atoms relative to copper atoms in stoichiometric structure of CuO compound and this effect
may convert the type of conductivity in the semiconductor [19]. These results match with other references [8, 10, 11]. This effect also leads to enhancement in mobility and carrier concentration as a result of reduced grain boundaries and improved crystallite size [20, 21]. The mobility values are approximately in the same order before and after heat treatment.

The DC conductivity measurements were used to study the activation energy with annealing temperature. The activation energy was calculated using the relation [19]:

$$\sigma = \sigma_0 \exp \left( \frac{E_a}{kT} \right)$$

Where, $\sigma$ is the conductivity as a function of absolute temperature $T$, $\sigma_0$ is the value of conductivity at $T=\infty$ (theoretically), $k$ Boltzmann constant, and $E_a$ is the activation energy. The variation of $\ln \sigma$ with $(1000/T)$ is presented in Figure 5. Table (3) shows the activation energy values against the annealing temperatures for CuO thin films. The activation energy values decreased and this means that the levels approached the conduction band and thus increase the conductivity values, thus rustle are disagree with [22]. But we confirmed by the energy gap values, which are increasingly observed in Figure 3 that means that energy level are approaching to conduction band level and therefore electrons need less activation energy to travel. Conductivity values increase with increase of annealing temperature, but when annealing at 600 °C it decrease because the probability of approached to the valence so the conduction is converting the semiconductor p-type to n-type and thus provided by Hall measurements.

### Table 2. Hall Effect parameters for copper oxide films before and after annealing.

| T(ºC) | Carrier concretion (cm⁻³) | $R_H$ (cm²/ºC) | $\mu_H$ (cm²/V.s) | $\sigma$ (Ω.cm)⁻¹ | Type of film |
|-------|--------------------------|----------------|------------------|------------------|---------------|
| 400   | 7.4×10¹⁷                | 8.4            | 1.005            | 0.119            | p-type        |
| C1    | 500                      | 7.6×10¹⁷       | 8.1              | 1.015            | 0.122         | p-type        |
| CA1   | 600                      | -8.5×10¹⁷      | -7.3             | -1.007           | 0.136         | n-type        |
| CA2   | 600                      |                |                  |                  |               |               |

### Table 3. Activation energy values and conductivity of CuO thin films.

| T(ºC) | $E_g$ (eV) | $E_a$ (eV) | $\sigma$ (Ω.cm)⁻¹ |
|-------|------------|------------|------------------|
| C1    | 400        | 2.45       | 0.25             | 21.11             |
| CA1   | 500        | 2.55       | 0.19             | 50.4              |
| CA2   | 600        | 2.6        | 0.16             | 26.4              |
Figure 5. Activation energy for CuO at 400°C, 500°C and 600°C.
The dc conductivity is also calculated using Four Point Probe device at room temperature for the samples prepared at 400 ºC and annealed at 500 ºC and 600 ºC. It was found that the conductivity increases (19.2, 38.4, and 34.4 Ω⁻¹.cm⁻¹) for the samples deposited at 400 ºC and annealed at 500 ºC and 600 ºC respectively. The increases agglomeration of crystalline volume and reduces the defects as established when examining XRD, and that means resistivity decrease, these result agree gated with [18].

4. Photovoltaic effect

As an optoelectronic application the CuO thin films (n-type) annealed at 600 ºC are used to fabricate n- CuO/p-Si heterojunction. It shows current density (J) against bias voltage (V) curve under dark and illumination conditions. The behavior identical to that of regular p–n junction. Here, the silicon base resistivity (10Ω.cm) is much greater than that of the CuO. Therefore, we expect wider depletion region width inside the silicon side since the carrier concentration is much than that of the n-type CuO according to the relationship:

\[ nX_n = pX_p \]

where \( n \) and \( p \) ( \( X_n \) and \( X_p \) ) are the depletion region (concentration of electrons and holes) for the and sides respectively. Thus, p-type silicon substrate with low conductivity may provide the material of choice to be used as a substrate in n-CuO/p-Si heterojunction solar cell [12].

Figure 6 shows the Current–Voltage curves of the n-CuO/p-Si HJSC under dark and illumination conditions. The curves are analogous to that of rectifying contacts. Moreover, the current under illumination condition in the reverse bias is always larger than that under dark condition. This illustrates that p-CuO/n-Si junction can be used to generate a photocurrent and there is an active depletion region between the two sides of the junction.

![Figure 6. I-V curve of n-CuO/p-Si heterojunction in the dark and illuminated.](image_url)
As seen in Figure 7, the obtained parameters for n- CuO/p-Si HJSC are listed in Table (4), and the result we obtained are similar with [21], who fabricate p- CuO/n-Si HJSC. So we can use poor solar cell pn from the same marital.

### Table 4. n- CuO/p-Si HJSC parameters.

| $J_{sc}$ ($\mu$A/cm$^2$) | $V_{oc}$ (V) | $R_s$ (Ω) | $R_{sh}$ (kΩ) | F.F | η (%) |
|-------------------------|-------------|----------|--------------|-----|------|
| 22                      | 0.0073      | 111      | 7            | 0.77| 1.24×10$^{-4}$ |

**Figure 7.** Efficiency solar cell n-type semiconductor CuO/p-type Si.

**Conclusions**

CuO thin films of p-type conductivity prepared by spray pyrolysis can be converted to n-type conductivity using a relatively high annealing temperature (600°C). This property can be used to prepare n-CuO/p-Si HJSC with 1.24×10$^{-4}$% efficiency.

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