The effect of substrate temperature on the physical properties of copper oxide films

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Abstract. The effect of the substrate temperature of the deposition of copper oxide prepared by chemical spray pyrolysis technique was studied. The XRD measurements show that all the films are polycrystalline structure with predominant phase(-111). The crystallite size increase with increasing substrate temperature. The AFM images in 1-D and the 2-D shows that the CuO nanostructure were in the shape of curly sticks growing in a vertical column at an average height of 2.00 nm and an average radius of 40 - 50 nm. These nanostructures of the 3% sample gets higher up to 9.00 nm. The value of the optical energy gap was calculated through the UV-Vis spectrometer and found to decrease with increasing the substrate temperature from 1.93 eV to 1.68 eV. Transmittance values also decreased from 79.5% to 36%.

Key word: CuO, Thin films, Optical properties, Spray pyrolysis, substrate temperature, photon energy graph, XRD, AFM.

1-Introduction

The development of solid semiconductors from metal oxides and the manufacture of semiconductors with n-type or p-type conductivity such as copper oxide and its use in the fields of pn-junction and transistors such as SrCuO2, CuGaO2 and CuAlO2 [1]. In particular, copper oxides are one of the important semiconductors in the manufacture of a hybrid junction and in the manufacture of solid gas sensors. They can be used as electrodes in many applications and can be used in solar cells [2], as well as as a superconductivity and as a high-absorption application for solar radiation [3], as well as low thermal emission [4]. Copper oxides have important characteristics such as low costs, abundance and non-toxicity [5]. Copper oxides exist in both Cuprous oxide, CuO monoclinic structure (1.9 eV  E_g  2.1 eV) [6] and Cuprous oxide CuO2 with a cubic structure (2.1 eV  E_g  2.6 eV) [7]. Copper oxides have been prepared...
in many ways, such as RF and DC reactive sputtering [8], thermal evaporation [9], Ion beam sputtering [10] and spin coating [11]. Copper oxides are considered by way of SPT to be the most common and easy way to manufacture solar cells. Muhammad Kaif et al. Study the impact of the temperature of the bases of silicon and its way PLD on the properties of copper oxide that the films recorded temperature of the room is random installation, and The increase in the temperature is transformed into a high crystallization with high orientation (200). It was found that increasing the crystalline volume with increasing temperature. The AFM measurements showed an increase in surface roughness with increasing temperature and decrease in energy gap values with increasing gradient [12]. S. Kosea et al. study the effect of temperature rules in the preparation of membranes copper oxide ultra spray pyrolysis USP and the manufacture of solar cells can be adopted this way for the low cost and simplicity in the manufacture of cells with high efficiency and explained the synthetic measurements improved crystallization with increasing temperature Surface measurements showed increased surface loading with increased temperature and high viscosity for the resulting films [13].

2-Materials and Methods

CuO thin films were deposited on glass substrates via chemical spray pyrolysis technique. Aqueous solution was maintained by dissolving 0.1 M of Copper (II) chloride dehydrate in distilled water to get a starting solution. This solution was sprayed by a homemade sprayer nozzle the optimum conditions in order to obtain well adherent films, free from pin holes, were: the nozzle was positioned at 28 cm above the substrate with the substrate temperature of (350°C, 450°C, 550°C), flow rate 5ml/min, spray period 10s lasted by 2 min to prevent immoderate cooling, Air was used as a carrier gas keeping at 10^5 Pascals. Film thicknesses were estimated by gravimetric method and was found to be about 350 nm thick. Transmittance and absorbance spectra for the prepared films were recorded using a UV-1650 spectrophotometer (SHIMADZU, Japan) as a function of wavelength ranging from 300 to 1100 nm. The structural properties were evaluated by XRD (Shimadzu, model: XRD-6000, Japan) with CuKα radiation (λ=0.154056nm). This process was done at room temperature and the 2θ value were varied in the range of 2θ = 20-60°. Surface topology of the as deposited films was obtained by AFM (AA 3000 Scanning Probe Microscope).

3-Result and discussion

Figure (1- a, b, c and d) represents the X-ray diffraction pattern of copper oxide, zoom in for the reflection of the dominant, the international card of the copper oxides and the dominant plane of reflection in the respectively, of the membranes prepared by the chemical spray pyrolysis method with different temperatures of the substrate (350, 450 and 550)°C. Note from Figure (1- a) that all films are polycrystalline and the dominant orientation of all temperatures is (-111) at the angle 2θ = 32.23°. And that this trend increases the intensity of the reflection with increasing the temperature of the rules during the preparation, accompanied by an increase in the crystalline size, which was calculated from the equation Scharr (1). Note from Figure (1- b) Angle deviation of the dominant reflection towards smaller 2θ values And the drop in the FWHM values, [14]. As the substrate temperature increases from 350°C to 550°C, Which was calculated from the equation of Shearer (1). The number of secondary reflections is (110), (-202), (-113) and (311) combined with angles, 32.5°, 72.43°, 61.54° and 48.74° and the intensity of these reflections increases with increasing the substrate temperature. The recorded films were shown to be highly consistent in the dominant reflection and with the same intensity of 100% with the international card No. 00-04-0245 as in Figure (1-d).
Where D is the crystallite size, λ is the x-ray wavelength (λ = 0.14506 nm), θ is the line broadening at FWHM (full width at half maximum intensity), ω is the Bragg angle and K is the shape factor, when K is unknown and cannot be determined, 0.9 is used as a good estimate, the coefficient K depends on such factors such as the geometry of crystallites. Figure (2) represents each of the FWHM, Crystalitesize, Microwstrain and Dislocation density as a function to the substrate temperature, It notes the inverse relationship between Crystallite size and other parameters. Table (1) represents some of the structural values of CuO at different substrate temperature.

\[ D = \frac{K\lambda}{\theta} \]  

Figure 1. (a) X-Ray diffraction pattern, (b) Zomm in image of the dominant reflection, (c) The international card of the copper oxides and (d) The dominant plane.
Figure 2. FWHM, Crystalites size, Microw strain and Dislocation density as a function to the substrate temperature.

Table 1. Structural values of CuO samples

| Samples | (hkl) Plane | 2θ (°)  | FWHM (°) | (D) (nm) | Microstrain (Line m−2) x102 | Dislocation Density (δ) (Line. m−2) x1015 | a (Å) |
|---------|-------------|---------|-----------|--------|---------------------------|---------------------------------------------|-------|
| 350°C   | (-111)      | 35.34   | 0.224     | 35.34  | 9.309                     | 8.004                                       | 4.140 |
|         | (-111)      | 35.33   | 0.201     | 39.34  | 8.345                     | 6.458                                       | 4.140 |
| 550°C   | (-111)      | 35.25   | 0.187     | 42.291 | 7.763                     | 5.590                                       | 4.140 |

Figure (3a, b, and c) represents two-dimensional images and a diagram of the distribution of atoms by their diameters and three-dimensional images of the CuO membrane recorded by chemical spraying of 350°C. Note from Figure (1- a) that nano-shaped structures in the shape of rods are sticking up to the top and the height of these sticks shape like is 3.75 nm and the diameters are 80-100 nm. In Figure (3- b) note that the largest percentage of diameter of 50 nm particles is 19%, followed by 15% for particles with diameters of 65 nm. And notes of Figure (3- c) which represents a three-dimensional image of developing membranes in different of highest and diameters, the average roughness are about 2.6 nm And the average particle size is 70 nm and R. M.S. is 2.63 nm.
As for the models deposited at 450°C, it is observed in Figure (4- a) that the number of the rod is more widespread compared to the models 450°C with a decrease in height to 2 nm, and the diameter is about 70- 80 nm. Figure (4- b) is the highest proportion of atoms with diameters 60 nm and the 80 nm and its approximate proportions Up to 11%. Either Figure (4- c) represents a three-dimensional image and can be seen the increase in the number of sticks growing and decreasing in average diameter. The average roughness are about 2.28 nm And the average particle size is 75 nm and R. M.S. is 3.00 nm.

Figure (5- a, b and c) represents two-dimensional images, Diametre percentage distribution particles and three-dimensional image. The record at a temperature of 550°C and notes of Figure (5- a) an increase in the height of the rods to grow to 9 nm and increase the diameter to 100 - 120 nm and note that it became less widespread than the previous model of 450°C. Figure (5- b) represents the percentage of the distribution of atoms by their diameter, and it is noted that the largest percentage is 12% is for particles of
65 nm and 70 nm. And Figure (5- c) shows, three-dimensional and notes through which the increase in height and diameters as well as sticks becomes more regular in the distribution and shape. The average roughness 2.87 nm and the average particle size 80 nm and R. M.S. 3.24 nm.

Figure 5. CuO thin film deposit at 550 °C, (a) 2-D image, (b) diameter distribution percentage and (c) 3-D image.

Figure (6) represents the spectrum of access to (350, 350 and 450) °C models, including a significant decrease in penetration from 79% to 36% when moving from a temperature of 350 °C to 450 °C. Note that the spectrum values were in the UV-Vis range. Regions due to the increased crystallization and dispersion of the spectrum at the grain boundaries [15].

Figure 6. transmittance spectrum of CuO thin films deposited at different substrate temperature.
Figure (7) represents the relationship between the photon energy and alpha (αhθ) and can be calculated from optical spectrum and by drawing the relationship between photon energy and h as shown in Figure 5 where the tangent of linear behavior can be drawn from Curved and intersected with the x-axis. The optical energy band gap Eg can be calculated according to Tauc formula:

$$\alpha h \theta = A(h \theta - E_g^0)^n$$

(2)

Where is the absorption coefficient, h is Planck’s constant, A is a constant and $E_g^0$ is the optical band gap, respectively. $E_g^0$ can be obtained through extrapolating $(h \theta)^2$ vs. photon energy ($h \theta$). Where the observed decrease in the values of the energy gap by increasing the values of the energy gap from 1.938 eV to 1.730 eV and then to 1.685 eV when increasing the temperature of the substrate from 350 °C to 450 °C and then to 550 °C respectively. The reason is due to improved crystallization and thus the CuO films are reduced to defects that result in dispersion of the falling rays [16].

The inset figure represent the brellouin zone the blue curved for the 350 °C and the red curved for the energy gap decreases for 550 °C.

4-Conclusions

We conclude from the research that the effect of the substrate temperature on the properties of the microstructure of copper oxide is prepared in the SPT. The structural properties are improved by increasing the intensity of reflection and decreasing FWHM with the shift of the preferred angle of reflection towards the smaller angles, with the growth of nano rods, whose number, height and diameter increase with the increase in the substrate temperature. We also infer a decrease in the values of the transmittance and values of the optical energy gap.

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