Preparation, Characterization And Optical Properties Of Copper Oxide Thin Films

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***Abstract*—Copper Oxide was deposited on glass slides as a substrate by the drop casting method at room temperature with a thickness of films (235and400)nm. The films were thermal treated at (500ºC) for one hour. The structural properties were diagnosed by using X-ray diffraction (XRD), the pattern of diffraction showing that the deposited films are polycrystalline in nature, the inter-planar spacing (d) and the grain size were calculated. The obtained results showed that the grain size increased with the increasing temperature. An atomic force microscopy technique (AFM) was used to measure the roughness of the prepared samples. The optical properties have been studied by using (UV-VIS) spectroscopy and Tauce's Method. The results show that the energy gap of 400 nm thickness of CuO thin film decreases when the films thermal treated at 500ºC from (2 to 1.68) eV, also increases with the increase of thickness, also the transmittance decreased after thermal treatment. The samples tested by optical microscopy to choose the best sample without any cracks.**

Keywords—Copper Oxide , Tauce's Method , thin film , XRD

1. Introduction- Copper oxide is an important semiconductor material with superconductivity properties, having immense application in sensors, field emission and photonic devices [1,2].It can be obtained from metallic copper oxidation and it is a p- type, that's mean the most carriers charge is holes [3]. There are two types of copper oxide, the first is a tenorite or cupric oxide, it is considered a stable type of copper It has polycrystalline structure and crystalline monolithic installation [4]. It is characterized by being the dark brown color and has a non-toxic and odorless nature as well as the possibility of availability and ease of production at low cost [5,6]. It has an Energy gap between the nearby visible and infrared spectrum with values (1.21-1.51eV) [7]. The Second type of copper oxide is cuprite or cuprous oxide [8], it is less stable than the first type and is a crystalline powder brown depending on the method of preparation and the size of the crystal. It is characterized by being a cubic shape and its energy gap values (2.1-2.6eV).It is used in photovoltaic complex requiring high efficiency [5, 8], good range of stability and high absorption in the visible wavelength range.

2. Deposition of Thin Films by Drop Casting Method

The solution of copper oxide was prepared from 1.5g copper nitrate ($Cu (NO_3)_2.2H_2O$), it is dissolved in 50 ml of (1%wt) PVP (poly vinyl propylene). The solution was added into a round - bottom flask with stirring. The mixture becomes blue color, then adding about 15ml of NaOH of (1M) to the solution, a nano - powder suspension was formed and kept at 75ºC for one hour, after that the particle washed with distilled water to remove any contaminations. The prepare solution shown in Fig. (1) Was deposited on glass slides as a substrate with (1.00*1.5) cm^2 area. They were cleaned with alcohol to remove the impurities and residuals from the surface. The optical absorption of the colloidal CuO was measured using Spectro photo- meter (Cary, 100(ONC Puls, UV-VIS-NIR, Split-beam Optics, Dual electors) in the range of (200-900) nm using quartz vessel. The structural properties of the deposited thin films at room temperature were studied by using X-ray diffraction (XRD-6000, Shimadzu X-ray Diffractometer), we can get information about grain size, lattice parameter, crystal structure like phase crystalline . The average grain size and roughness of CuO were investigated by using AFM (AA3000 scanning probe Microscope). The sample was examined with the optical microscope (Nickon Eclipse-ME600) to select the best samples without sharp edge and cracks.

Figure (1): Image of CuO Nanoparticles Colloidal dissolved in PVP.

The inter planer distance (d) for different planes were measured by Bragg's law [9,10]:

$$2d\,sin\,\theta = n\lambda \qquad (1)$$

Where: (n) is the reflection order, (d) estimated from the relation (2)[11]:

$$(1/d^2)=(h^2/a^2sin^2\beta)+(k^2/b^2)+(l^2/c^2sin^2\beta)+(2hlcos\,\beta/acsin^2\beta) \qquad (2)$$

The grain size dimension diffraction could be calculated from Debye-Scherer formula (XRD) as in equation (3)[12]:

$$D = K\lambda/\beta\cos\theta \qquad (3)$$

Where: (K) is the shape factor and equal (0.94), (θ) is the diffraction angle (λ) is the x-ray wavelength and (β) is the line broadening.

For optical parameters the Transmittance denoted (***T***), (**α**) Absorption coefficient, (***t***) thickness of films, (**Eg**) Energy gap, **E(hν)** Photon energy (eV) The photon energy (hν) can be calculated using equation(4)[13] :

$$E(eV) = 1240/\lambda(nm) \qquad (4)$$

The value of absorption coefficient (α) was determined by the equation (5) [13] :

$$\alpha = 2.303A/t \qquad (5)$$

3. Result and Discussion

3.1Structural Properties Measurements:

X-ray diffraction (XRD) studied by using X-ray diffractometer (XRD-6000, shimadzu), analysis of diffraction spectra indicates the peak position for CuO films of 235nm thickness. As evidenced from Fig.(2) the relationship between the intensity of x-rays and Bragg's angle for the copper oxide film deposited on the glass slide that there are narrow distinct peaks corresponding to diffraction angle (33º,35º,38º,67º) and diffraction from planes of the (110), (002), (111) , (310) for CuO and (111) for Cu_2O at diffraction angle (47º) reported by refs [14] . the lattice parameters for monoclinic CuO a=4.688(4)Aº,b=3.4229(2)Aº,c=5.1319(3)Aº, it is represents the copper oxide pattern according to the international standard card (00-035-1091).

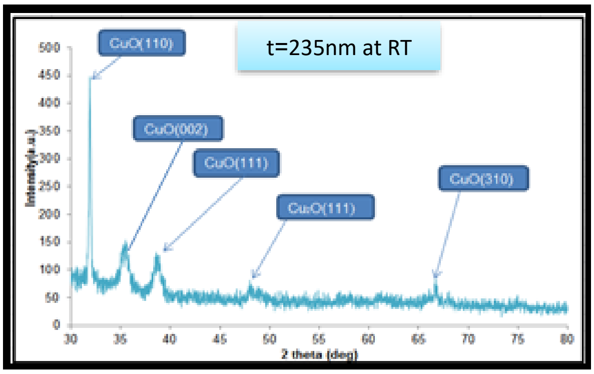


Figure (2): X-ray pattern of copper oxide thin films prepared on glass substrate with thickness (235nm) as deposited.

It is clear from Fig.(3) when the film treated thermally at high temperature 500ºC the Cu_2O bond is broken and another phase appears $(20\bar{2})$that's mean that the film becomes more crystalline and the phase (110) change and disintegration because of the weak bond between the grains. The grain size decreases, crystallization increases and Miller indices change due to change of phase from the cubic to monoclinic after applying high temperature , this result according to the international standard card (00-044-0706). From the results obtained from the patterns of diffraction indicate that the deposited films are polycrystalline in nature[15].

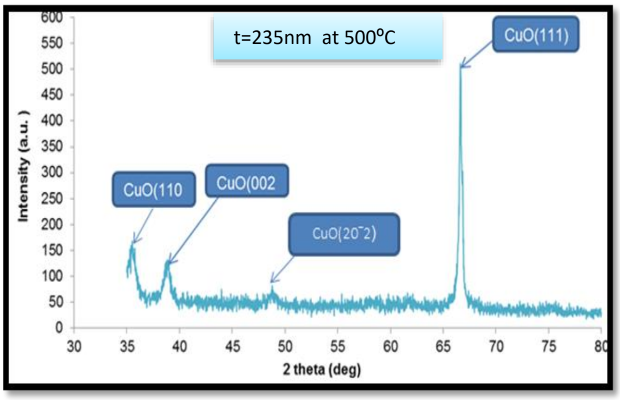
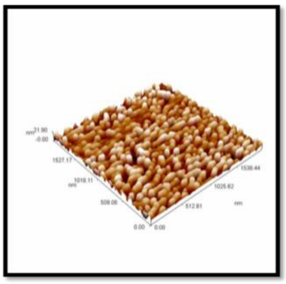
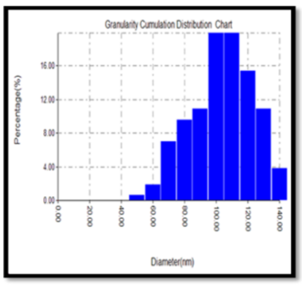


Figure (3): X-ray pattern of copper oxide thin films prepared on glass substrate with thickness (235nm) after thermal treatment.

The morphology, roughness and grain size were investigated as shown in Fig. (4) by using atomic force microscopy (AFM). It was found that the roughness of CuO thin film of thickness (235nm) is (0.589nm), the average grain size is (70.36nm) and the root means square is (0.746).





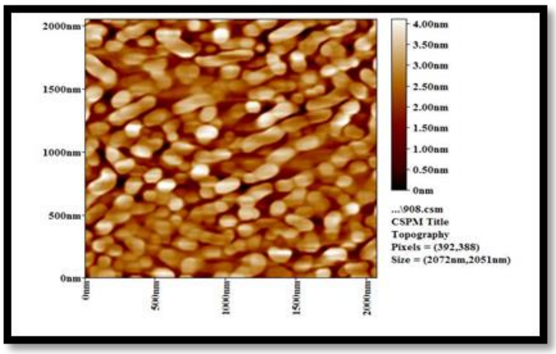


Figure (4): AFM Images for copper oxide thin film of thickness(235nm) .

3.2 Optical measurements

From the results obtained by using (UV-VIS) spectroscope, the transmittance has been studied. Fig.(5) shows the relationship between the transmittance spectrum and the wavelength for the CuO thin films deposited on glass substrate , it is clear from figure that the transmittance was increasing with the increased of wavelength and decreasing after thermal treatment at 500ºC temperature while, when the thickness of films was increased the transmittance was decreasing .

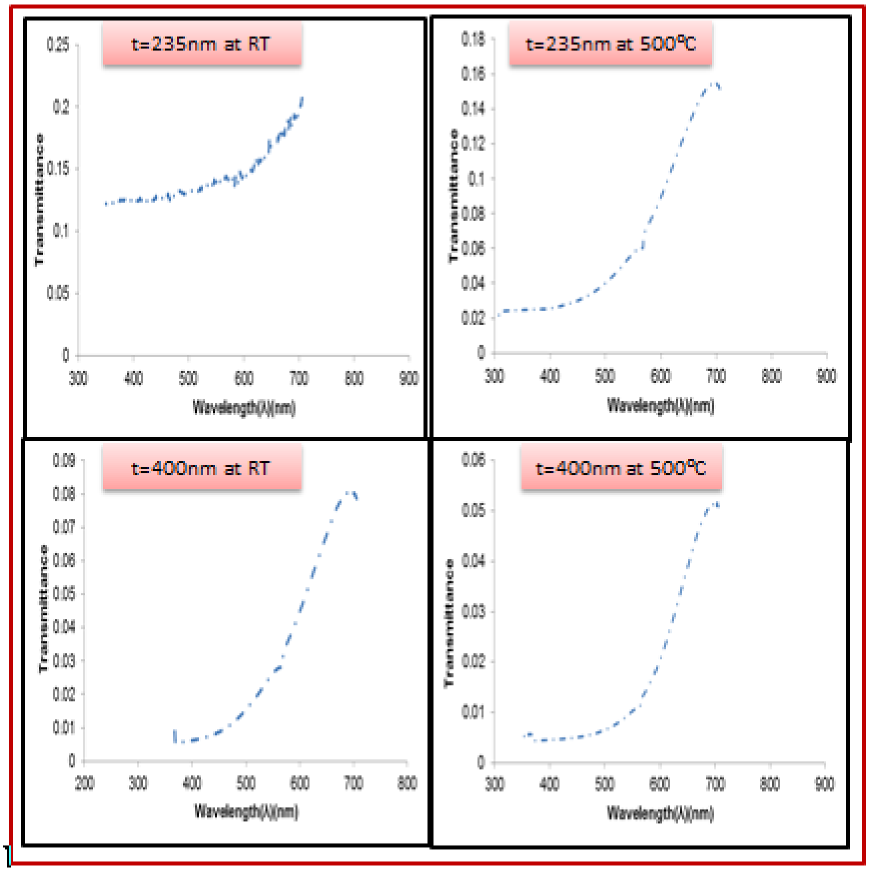
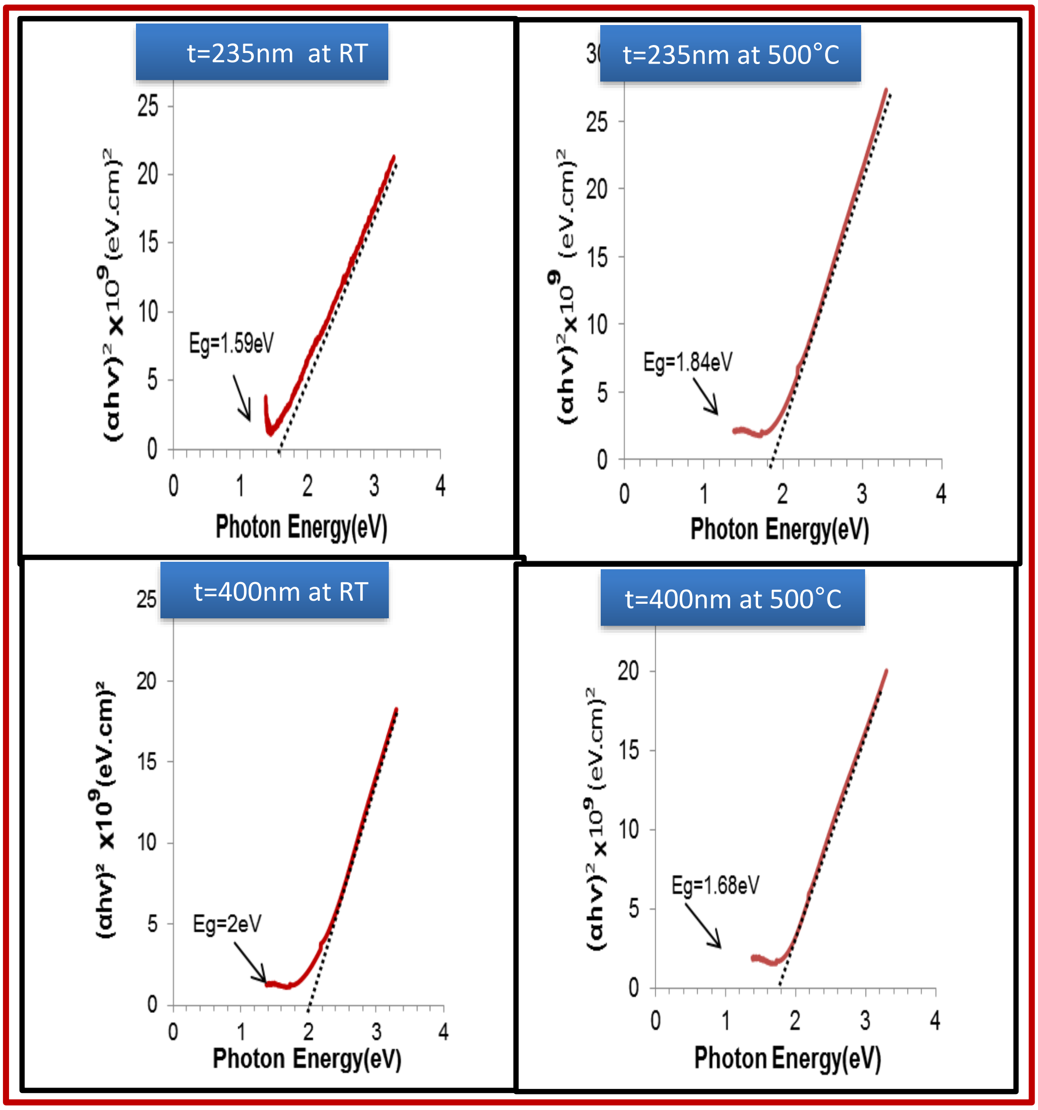


Figure (5): the relation between the transmittance and the wavelength before and after thermal treatment.

The energy gap for the allowed direct transmittance is calculated by plotting the relationship between $(\alpha h\nu)^2$ and the photon energy; for thickness (235nm) it is increased after thermal treatment because that the high temperature increases the crystalline size of the thin film and decreases crystalline defects , resulting in a decrease in the levels of the defect within the energy gap, so that the energy gap increased, this can be attributed to the change of lattice constant or to the change of thin film composition from cubic phase to monoclinic phase [14] . For the thickness (400nm) we notice that the energy gap decreased and this can be explained by the increase in thickness led to a clear increase in the number of photon collisions with the material and this will lead to an increase in the number of electrons and holes leading to a decrease in the energy gap, the result agrees with the results of refs [15]. The value and type of energy gap depend on the material, its nature and the impurities in its composition [7]. Fig. (6) Shows this relationship.

3.3The Optical Microscope

Figure (7) represents an image of the (10*10) micro - dimensions of the copper oxide deposited on the glass slides with thickness (235nm), where it is noted that there are bright regions representing the nanoparticles distributed on the surface regularly with a high concentration interspersed with some holes black spots. This examination is to know are the film is distributed on the surface or not, and also to determine the suitability of the drop method to prepare the copper oxide film . It is note that the process of the Annealing at a temperature 500°C leads to increase the particle size in the rate of 3:1, with a sharp contrast and differentiation of the nanoparticles prepared, noting the presence of particles separate from each other and some are formed in the form of clusters or groups semi-circular.



Figure(6):The direct allowed energy gap for CuO thin films of thickness (235 , 400)nm at room temperature and 500°C from the relationship between $(\alpha h\nu)^2$ versus photon energy gap.

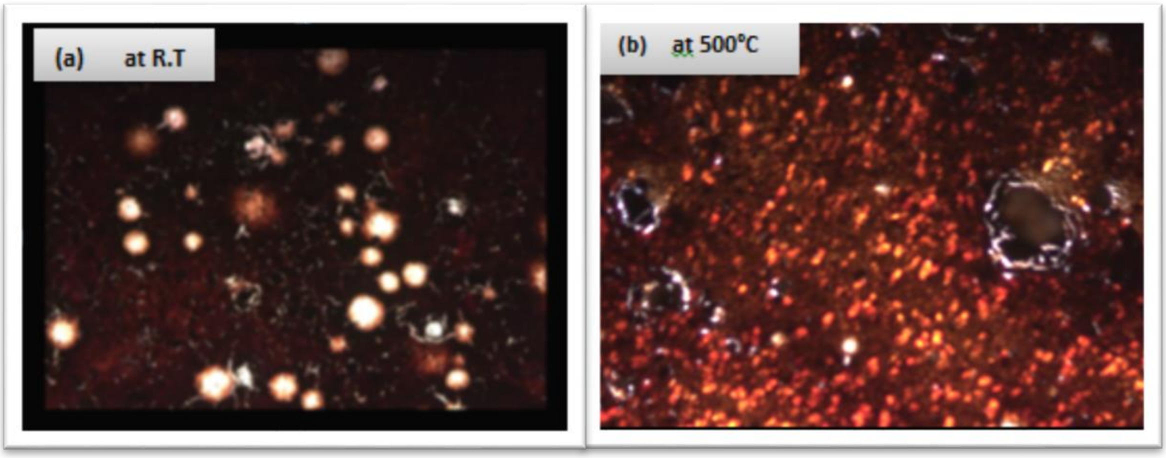


Figure (7): Image of optical microscope for copper thin film with thickness 235nm (a) at roo

Conclusion:

Copper oxide thin films at thickness (235,400) nm deposited by the drop casting method. In our research we studied in detail the influence of thickness and thermal treatment on the structural and optical properties. XRD diffraction patterns showed that the thin film polycrystalline, and has monoclinic crystal structure, also we noticed tetragonal and cubic phases, it is clear that the thermal treatment at temperature (500ºC) caused an increase in grain size, and the film become more crystalline, the tetragonal and cubic phases converted to monoclinic. The morphology , grain size and Roughness obtained from AFM microscopy, the results showed that the CuO thin film have spherical shaped with good homogeneous. The energy gap values increase with the thickness, and decrease after thermal treatment at (500ºC).Copper oxide have high transmittance in the near infrared region. The image of optical microscope revealed the cracks and needle grains getting agglomerated.

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