Effect of Aluminum Doping on Structural Properties of CuO Thin Films Prepared by Chemical Spray Pyrolysis (CSP) Technique

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Abstract

In this paper CuO thin films were prepared using chemical spray pyrolysis technique (CSP) with different dopant concentration of Al^{+3} (0, 3, 5 and 7)% at substrate temperature of (400 ^{o}C), and thickness of about (400±10) nm .The structural properties of (CuO: Al) thin films were studied using X-ray diffraction technique. The investigation through the above technique, appeared the structure of CuO which was of crystalline monoclinic and preferred orientation along (111) plane. Also the structural studies showed the decrease of average grain size with increase of (Al) dopant concentration were in the range of (12.57-11.69 nm). The structural parameters including dislocation density (δ), and number of crystal per unite area (N_o) were also calculated. The atomic force microscopes (AFM) results showed that the root mean square (RMS) and surface roughness increases with increase of (Al) dopant.

Keywords: CuO thin films, Aluminum, CSP, structural properties, doping

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تأثير التطعيم بالألمنيوم على الخصائص التركيبية لأغشية (CuO) الرقيقة المحضرة بتقنية التحلل الكيميائي الحراري (CSP)

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الخلاصة

تم في هذا البحث تحضير أغشية اوكسيد النحاس (CuO) الرقيقة المشوبة بعنصر (Al) و بنسب حجمية (0, 3, 5, 7 %) بطريقة التحلل الكيميائي الحراري، وذلك بترسيبها على قواعد زجاجية بدرجة حرارة (400 ºC) ، وسمك مقداره (400±10) nm. درست الخصائص التركيبية لأغشية (CuO: Al) باستعمال طريقة حيود الاشعة السينية، والتي أظهرت أن اغشية (CuO) ذات تركيب بلوري احادي الميل و باتجاه تفضيلي (111)، وبينت الدراسة التركيبية كذلك نقصان معدل الحجم الحبيبي مع زيادة التطعيم بالألمنيوم وبمقدار (12.57-11.69 nm)، الثوابت البصرية تضمنت حساب كثافة الانخلاعات (δ) وعدد البلورات لوحدة الحجم (N_o). اظهرت نتائج فحوصات مجهر القوة الذرية (AFM) ان كل من مربع متوسط الخشونة (RMS) وخشونة السطح تزداد مع زيادة نسب التطعيم بالألمنيوم .

الكلمات المفتاحية : أغشية اوكسيد النحاس الرقيقة، الالمنيوم، التحلل الكيميائي الحراري، الخصائص التركيبية، التطعيم.

Introduction

Cooper oxide (CuO) is monoclinic structure, p-type semiconductor with a narrow band gap of (1.3-2.1 eV) [1-3]. Copper oxide, which is a promising semiconductor material for fabrication of photovoltaic devices like solar cells [4]. Copper oxides were used for hydrogen gas sensors [5], and volatile organic compounds [6], photoelectron chemical cell [7], etc. It has been widely investigated for various applications such as solar energy conversion, optoelectronics, batteries, sensors, semiconductors, and catalysis [6, 7]. The nontoxicity of CuO and abundant availability of its constituents make it an advantageous and promising material for device applications [8], many efforts have been made to fabricate nanostructured CuO materials, including nanoparticles [9]. Several techniques such as: thermal oxidation, electro deposition,

spraying, chemical vapor deposition, plasma evaporation, reactive sputtering, and molecular beam epitaxy have been used to prepare copper oxide thin films [10]. In this study we report the effect of (Al) doping on the structural properties of CuO nanostructures thin films by chemical spray pyrolysis using X-ray diffraction (XRD), atomic force microscopes (AFM) techniques.

Materials and Methods

Pure and Al-doped CuO thin films were deposited on glass substrates by chemical spray pyrolysis technique as follows:

Solution of (0.1M) concentration for copper nitrate (Cu $(NO_3)_2.3H_2O$) was prepared by dissolving (2.416g) copper nitrate in (100ml) distilled water. Also a solution of cocentration (0.1M) of aluminum nitrate can be prepared by dissolving (3.7513g) (Al $(NO_3)_3.9H_2O$) in (100ml) distilled water depending. The (X-ray) diffraction patterns for the prepared thin films were obtained in a (Shimadzu XRD - 6000) goniometer using copper target (CuKα, 1.5418 Å) and Atomic Force Microscopy (AFM) micrographs were recorded by using scanning probe microscope type (SPM-AA3000), contact mode, supplied by Angstrom Advanced Inc. Optical properties in the wavelength range of (300-900) nm were investigated by using UV-VIS-NIR spectroscopy (Shimadzu, UV-1800).

Results and Discussion

The X-ray diffraction (XRD) investigation has been carried out for the pure and (Al) doped with CuO thin films. XRD patterns of the undoped and Al–doped CuO films are shown in Figure 1. The patterns indicate that all of the films have a polycrystalline and exhibited monoclinic phase of the prepared films according to (ICCD) card no. (05-0661). this is consistent with the study [11]. It is observed that the XRD patterns for all films show Bragg's angles at (2θ~38.730º, 35.541º, 35.553º, 53.411º , 68.140º and 32.520º) which are assigned to (111), (002), (-111), (020), (220) and (110) directions respectively. The relatively stronger peak intensity indicates preferential (111) orientation of the all thin films, and there are two peaks (020) and (220 are decreased dwith doping in (5, 7%). In addition to that, it is found,

that the position of the peak represented by the plane (111) is shifted toward left according to the ratio of doping, which explained in table (1). The intensity of the peaks decreased with doping , leading to improvements in the crystallinity of the derived films. This results may be due to the type of bond which formed among atoms for thin films.

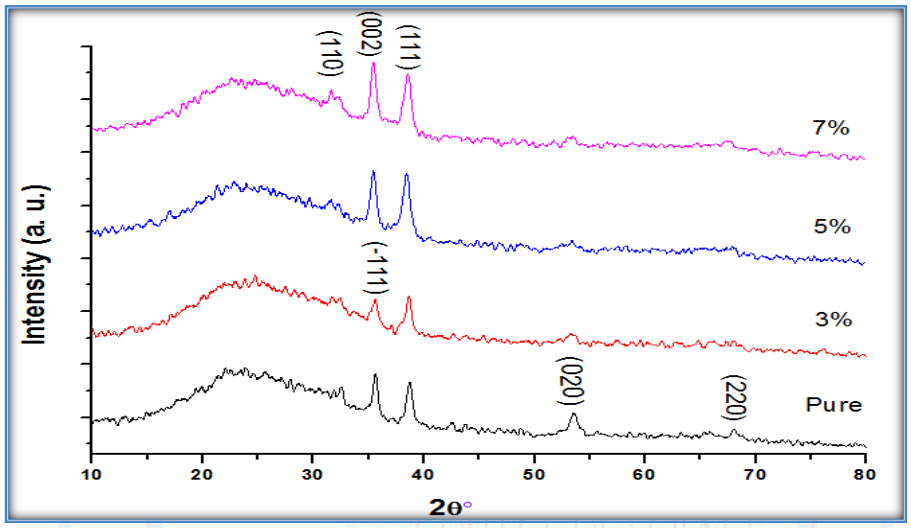

Fig.(1) X-ray diffraction pattern for the undoped and Al doped CuO

1- The average crystallite size

The average crystallite size for the films can be calculated for (111) direction by Scherrer formula by using the relation [12]:

$D_{av} = K\lambda / \beta \cos\Theta$……(1)

Where, D_{av} is the crystallite size, K is a constant known as Shape factor (= 0.94), β is the Full width at half maximum (FWHM) given in radians and θ is the Bragg's angle.

It is observed that the average crystallite size for the copper oxide thin films from the (111) peaks decrease when ratio of doping by Al increase, and the range of average crystallite size (12.57 – 11.69) nm shown in Figure(2). The decrease of average crystallite size in our samples shows that at least a small quantity of Al^{+3} ions substituted the Cu^{+2} ions, since the Al^{+3} ionic radius (0.53 °A) is smaller than that corresponding to Cu^{+2} ion (0.73 °A)[13]. as shown in Table (1).

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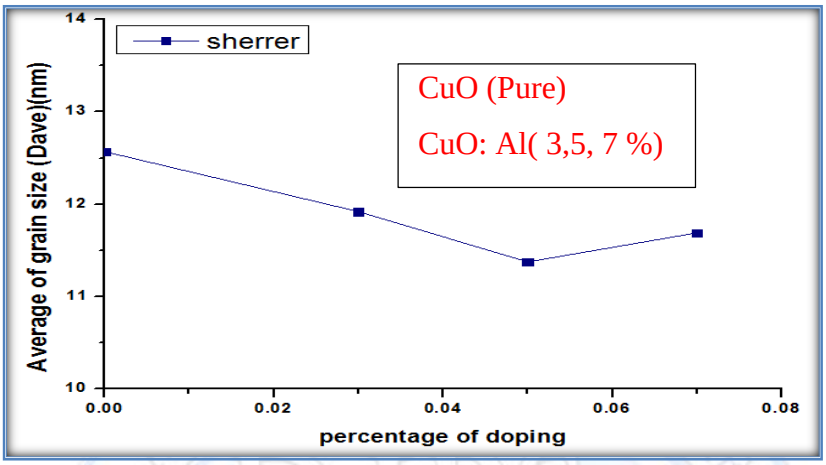

Fig.(2): Average grain for the undoped and Al doped CuO.

2- Dislocation Density

The dislocation density is the measure of amount of defects in a crystalcan be defined as the dislocation line per unit volume. The dislocation density (δ) can be calculated as the following [14]:

$$\delta = 1/D_{av}^2 \quad \text{.....(2)}$$

The small value of dislocation density obtained in the present work confirmed good crystallinity of the (CuO:Al) thin films fabricated by employing chemical spray pyrolysis technique. Dislocation density increase with doping by Al . Figure (3) show change dislocation density with ratio of doping, as shown in table.(1).

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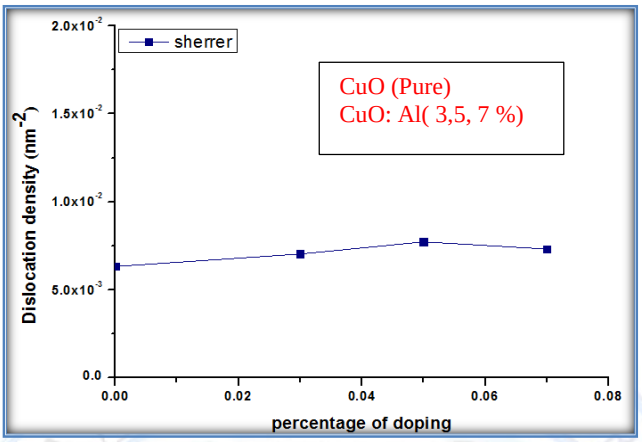

Fig.(3): Dislocation density for the undoped and Al doped CuO.

3- Number of Grains

The number of grain per unit area (N_o) can be calculated as the following [15]:

$$N_o = t / D_{av}^3 \quad \text{……..……..(3)}$$

Where t : is the film thickness.

It can be seen that the number of grain increase when ratio of doping by Al. Figure (4) show change number of grain with doping, as shown in table.(1).

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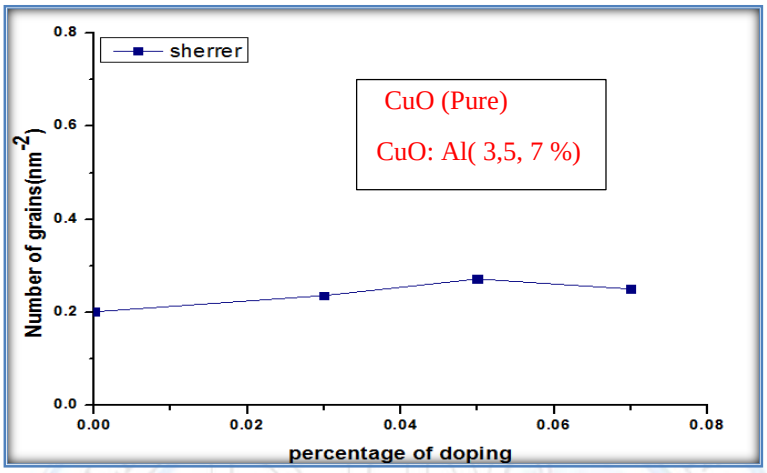

Fig.(4): Number of grains density for the undoped and Al doped CuO.

Table (1): Structural parameters of Al-doped Copper Oxide thin films

Sample	CuO	CuO:Al (3%)	CuO:Al (5%)	CuO:Al (7%)
2θ (deg)	38.6998	38.6282	38.4550	38.5149
d_{hkl}(Å)	2.32483	2.32897	2.33906	2.33556
FWHM(deg)	0.67000	0.70670	0.74000	0.72000
D_{av}(nm) Scherrer	12.57	11.92	11.375	11.69
δ (nm^{-2}) Scherrer	0.0063289	0.0070379	0.0077285	0.0073176
N_o(nm^{-2}) Scherrer	0.201398	0.23617	0.271773	0.25039

4-(AFM) Results

The atomic force microscopy (AFM), investigation have been carried out for the prepared pure and Al doped CuO thin films. The results showed that (RMS) and surface roughness increases with doping as shown in table(2), where adding Al considerably improves the surface smoothness by decreasing the grain size. Figure (5) shows the (AFM) images for pure and (CuO:Al) thin films.

Table (2):(RMS) and surface roughness and grain size for pure and doped with (Al) CuO thin films.

Sample	Surface roughness (nm)	RMS (nm)	Grain size (nm)
CuO	2.17	2.56	102.91
CuO:Al (3%)	3.36	4.08	95.37
CuO:Al (7%)	2.86	3.78	95.77

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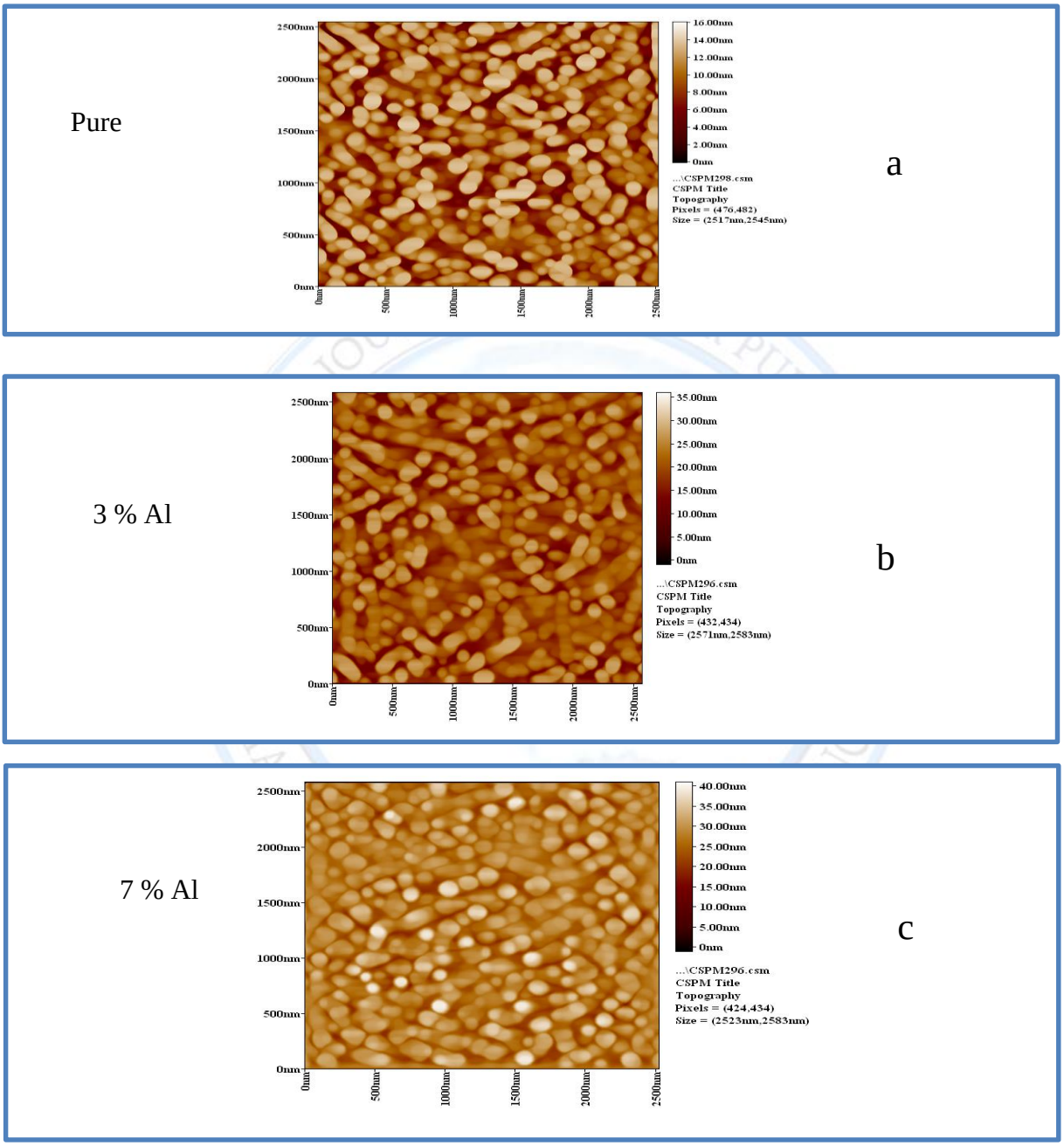

Fig.(5): AFM images for pure and Al doped CuO thin films.

(a) pure,(b) doping (3%), (c) doping (7%)

Figure (6) explain relation between (RMS) and surface roughness as function of percentage of doping percentage.

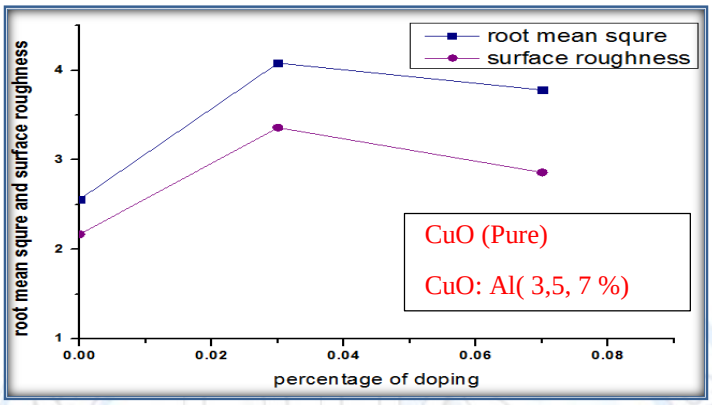

Fig.(6): relation between (RMS) and surface roughness as function of doping percentage.

Conclusions

XRD patterns of the undoped and Al–doped CuO films indicate that all of the films are polycrystalline with monoclinic structure. The main characteristic peaks are assigned to the (111). The average grain size for the Copper Oxide thin films decreases with increasing the Al-concentration. Dislocation density and the number of grains increases with Al-doping, also measurements of atomic force microscopes (AFM) showed the values of each of the surface roughness, root mean square (RMS) increases with Al- doping.

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