J Nanostruct 13(4): 1159-1167, Autumn 2023

RESEARCH PAPER

Investigation of Nanostructured Zirconium Oxide Films Manufactured by Spray Pyrolysis: Structural, Morphological, and Optical Properties

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ARTICLE INFO

Article History:
Received 11 June 2023
Accepted 20 September 2023
Published 01 October 2023

Keywords:
Cu doping
Morphology
Optical properties
Spray Method
ZrO_2

ABSTRACT

Nanostructured ZrO_2 and ZrO_2: Cu were prepared employing CSP method. XRD anaylsis assures that ZrO_2 offer the formation of crystalline phase with (200) plane by increasing Cu-doping. Crystallite size (*D*) increases from (15.990 -19.780) nm as copper content increase, whilst strain (ε) decreased from 2.160 to 1.750, whilst dislocation density (δ) reduction from 3.91 to 2.55. AFM technique was employed to know the film topography. The AFM have revealed that particle size observed was in the zone of (82.310 - 67.760) nm with Undoped ZrO_2 and ZrO_2: 3% Cu respectively, Whilst the root mean-square(rms) roughness from (5.830 - 3.210) nm of Undoped ZrO_2 and ZrO_2:3.0 % Cu respectively. E_g reduction from 5.2 eV before doping to 5.0 eV after 4% Cu-doping. Whilst absorption coefficient, Refractive Index and extinction coefficient are rising with rising with Cu content with ZrO_2 thin films.

How to cite this article
Ali1 H., Khaleel al Qaisy H., Mubarak H. , Karhib M., Abood E. Investigation of Nanostructured Zirconium Oxide Films Manufactured by Spray Pyrolysis: Structural, Morphological, and Optical Properties J Nanostruct, 2023; 13(4):1159-1167. DOI: 10.22052/JNS.2023.04.024

INTRODUCTION

ZrO_2 is promising material due to its god transparencyand thermal stability [1,2]. In recent years, zirconium dioxide (zirconia,ZrO_2) thin films, owing to excellent optical, thermal, mechanical and electrical properties [3–10], have been widely used in diverse fields, such as optical filters, anti-corrosion, protective and thermal barriers, gas sensor, anti-reflection coating [8, 9] and as insulators in microelectronic devices [10].Depending on deposition technique, its parameters and heat treatment, ZrO_2 films can exist in various phases, monoclinic, tetragonal, cubic and amorphous [3, 8]. Its own direct and indirect transition in (5.87) , (5.22) eV, respectively [9]. Several method for depositing ZrO_2 like; pulsed laser deposition [11], thermal evaporation method [12], sol-gel [13], RF sputtering deposition was employed [14] Plasma spraying [15], laser ablation [16], ECD [17], magnetron-sputtering [18], dip-

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coate [19] hydro-thermal processing [20], liquid phase deposition[21], and spray pyrolysis method [22-28]. spray pyrolysis method have control over the deposition rate, film. This work aims to deposit ZrO_2 films by spray pyrolysis method, This work aims is to study physical properties of undoped ZrO_2 and ZrO_2: Cu film.

MATERIALS AND METHODS

Nanostructured ZrO_2 films were deposited utilizing chemical spray pyrolysis technique. A solution containing 0.10 M ($ZrOCl_2.8H_2O$) , resolved oxalic acid in (100.0 mL) re-distilled H_2O. (0.10 M) of $CuCl_2.4H_2O$ was used a doping agent with a concentration of 2%, 4% to obtain Cu doped Zirconium oxide.. It began with a 400 °C starting point. Following criteria were used to evaluate the deposition conditions: It was 28 centimeters from the base to the spout. 10 seconds were spent spraying, at a rate of 4 milliliters per minute, with a 3 minute interval among each sprayer action. As a transport gas, N2 was used. ZrO2 thin film formation was verified by XRD analysis. Film-thickness was measured by weighing and was 35025 nm. To obtain film topography, (AFM) used . Transmittance and absorption measurements were performed using a dual beam UV-Visible spectrophotometer to evaluate the optical characteristics.

RESULT AND DISCUSSION

XRD styles in [Fig. 1]displays nanostructured ZrO_2 , ZrO_2:Cu thin film (thickness350 nm) is 31.46°, 34.25°, 49.26°, and 54.70° matched anatase

Table 1. Explain D structural parameters, and E_g of deposited films.

Samples	(hkl) Plane	2Θ (°)	FWHM (°)	*D*(nm)	Optical bandgap (eV)	Dislocations density (× 10^{15})(lines/m^2)	Strain × 10^{-3}
Undoped ZrO_2	200	34.25	0.52	15.99	5.2	3.91	2.16
ZrO_2: 2% Cu	200	34.00	0.47	17.68	5.1	3.19	1.96
ZrO_2: 4% Cu	200	33.96	0.42	19.75	5.0	2.55	1.75

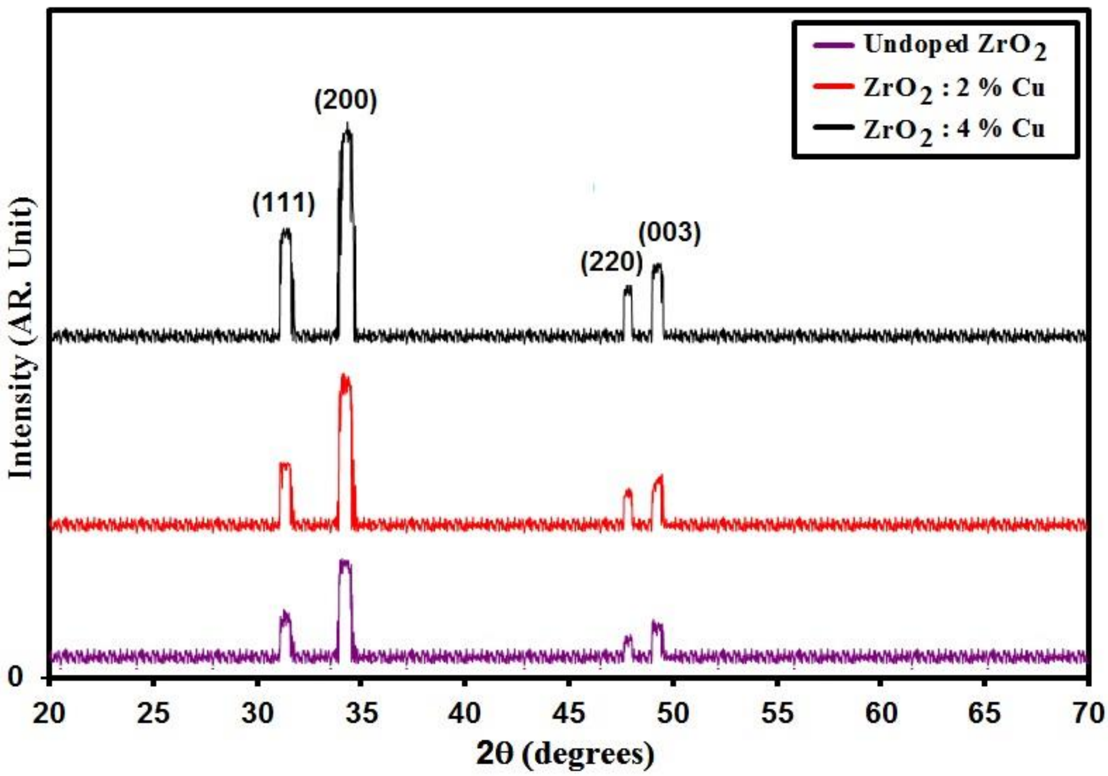

Fig. 1. XRD pattern of intended films.

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(111.0),(200.0), (220.0)

and (003.0) planes, respectively. Increase peak at (200.0) was seen that fit with(ICDD) card no 1314-23-4.

The average crystallite size (*D*) is obtained employing Scherrer's formula [29-31]:

$$D = \frac{0.9\,\lambda}{\beta cos\theta} \quad (1)$$

At which, β and θ are (FWHM) and (λ) is the wavelength of the X-rays employed (0.15410 nm), β and θ are (FWHM) and the diffraction angle, respectively. (Table 1) presents the obtained information. It was demonstrated that as copper content increased, D increased from (15.990 - 19.780) nm. Therefore, copper concentration is appropriate for determining the diameters of material crystals.

The relation [32–34] was used to determine the dislocation density (δ) in thin films

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

Table 1 explains that dislocation density (δ) lawering for (3.91 - 2.55).

information about material structure gives by the strain (ε), depend by employing the following equation [35-37]:

$$\varepsilon = \frac{\beta cos\theta}{4} \quad (3)$$

Table 1 explains that strain (ε) decreased from 2.16 to 1.75.

Fig. 2 offers FWHM, *D*, ε and *δ* vs. Copper concentration.

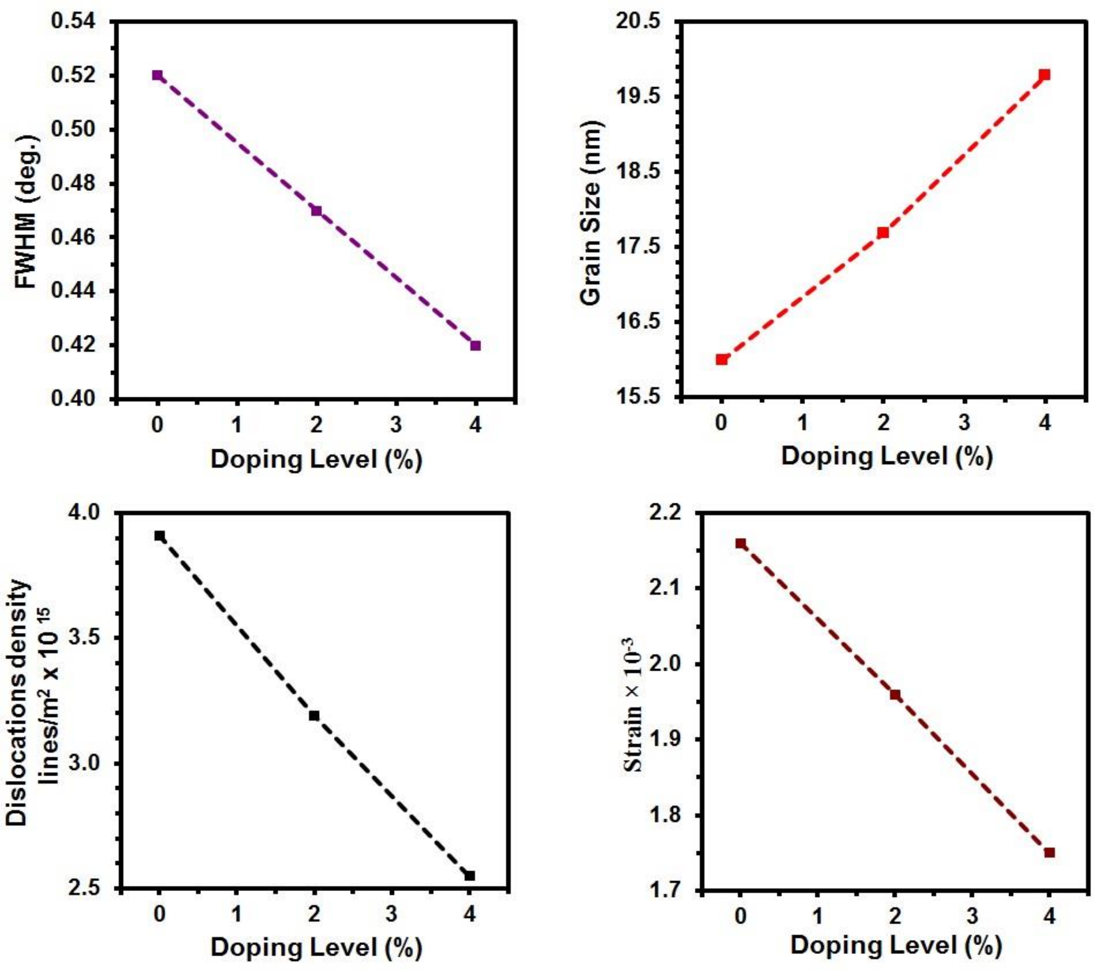

Fig. 2. FWHM (a) D, (b) δ, (c) ε,(d) of intended film.

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The 3D AFM surface images were shown in Fig. 3 (a1, b1 and c1). From these figures, it can be noticed that homogenous grain vertically aligned were observed. From Figure 3 (a3, b3 and c3) it can be noticed that The particle P_{av} size was in the zone of (82.31- 67.76) nm with Undoped ZrO_2 and ZrO_2: 3.0% Cu respectively, Whilst the (rms) roughness from (5.830 - 3.210 nm) of nanostructured ZrO_2 , ZrO_2: 3.0 % Cu respectively, according to the granularity cumulation distribution, their average values were shown in Table 2.

The wavelength range of the transmittance (T) spectra, which extend from 300 to 900 nm, is displayed in Fig. 4. All the ZrO_2 produced at 4% Cu doping showed Transmission values above 63% for Cu-doped thin films.

Using [38-40], we can calculate the absorption coefficient (α):

$$\alpha = \ln{(1/T)}/d \quad (4)$$

in which (d) is the thickness of the film.

Reduced with an increase at 2% or 4% doping, according to Fig. 5.

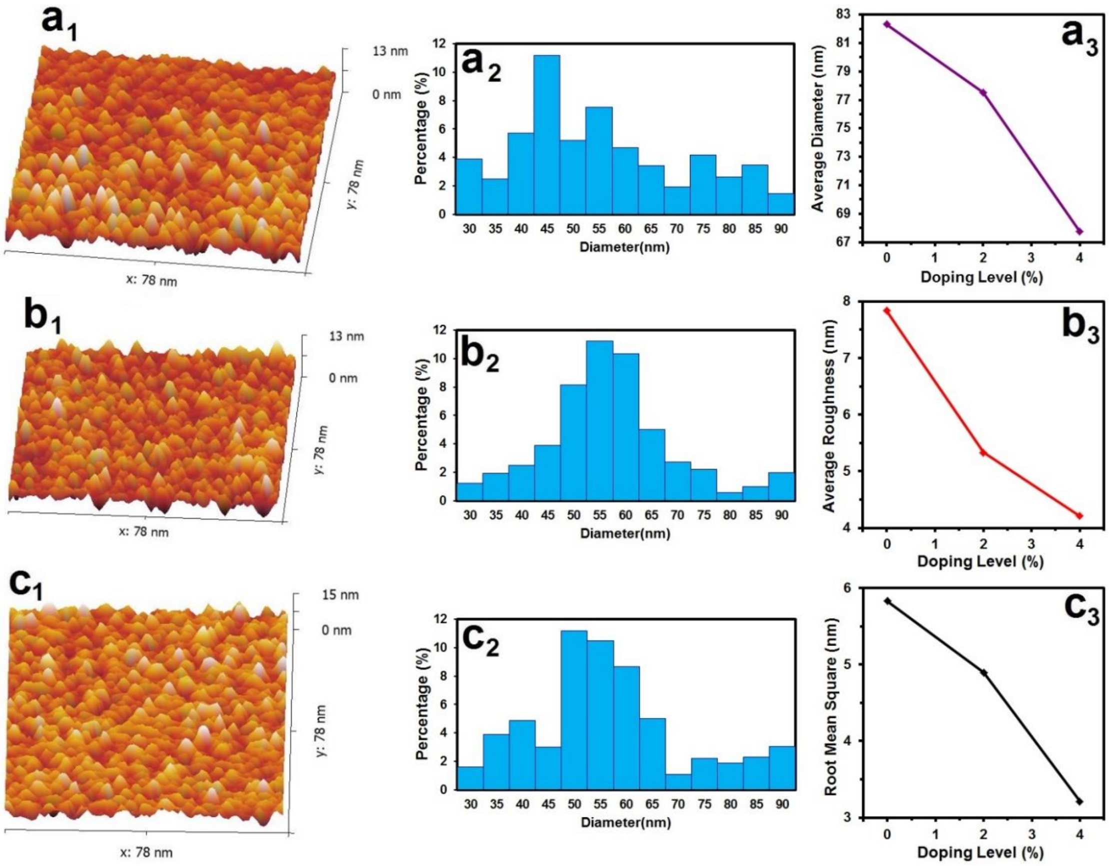

Fig. 3. AFM images of Undoped ZrO_2 and ZrO_2:Cu thin films with granularity cumulation distribution chart, and variance of AFM parameters against doping

Table 2. Explain AFM parameters of the intended films

Samples	P_{av} Nm	Ra (nm)	rms. (nm)
Undoped ZrO_2	82.31	7.84	5.83
ZrO_2: 2% Cu	77.54	5.33	4.89
ZrO_2: 4% Cu	67.73	4.21	3.21

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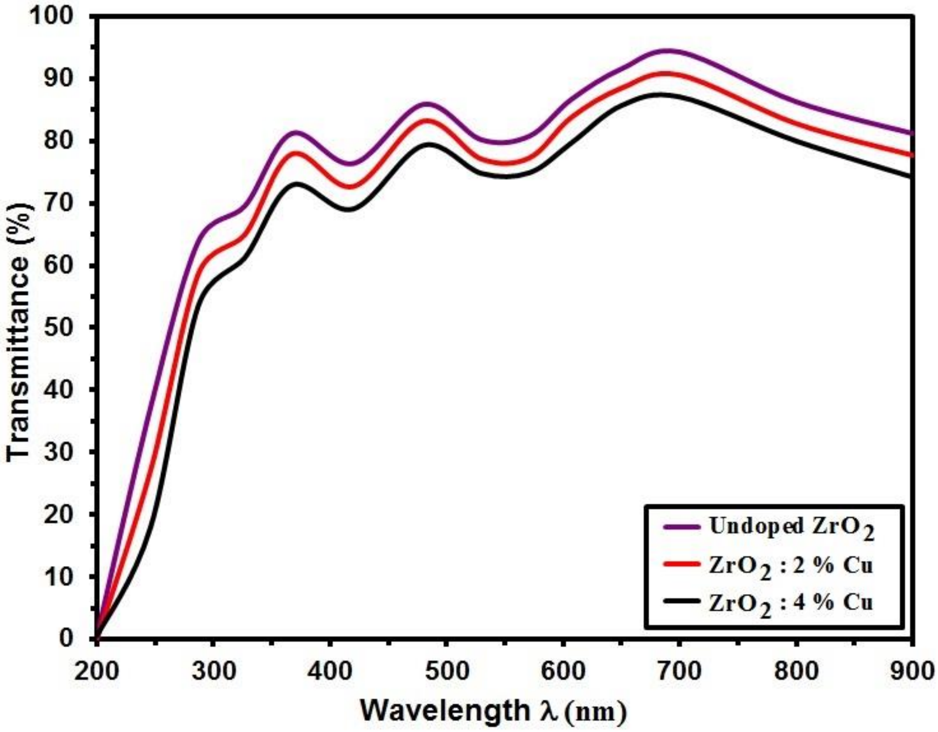

Fig. 4. T of prepared films.

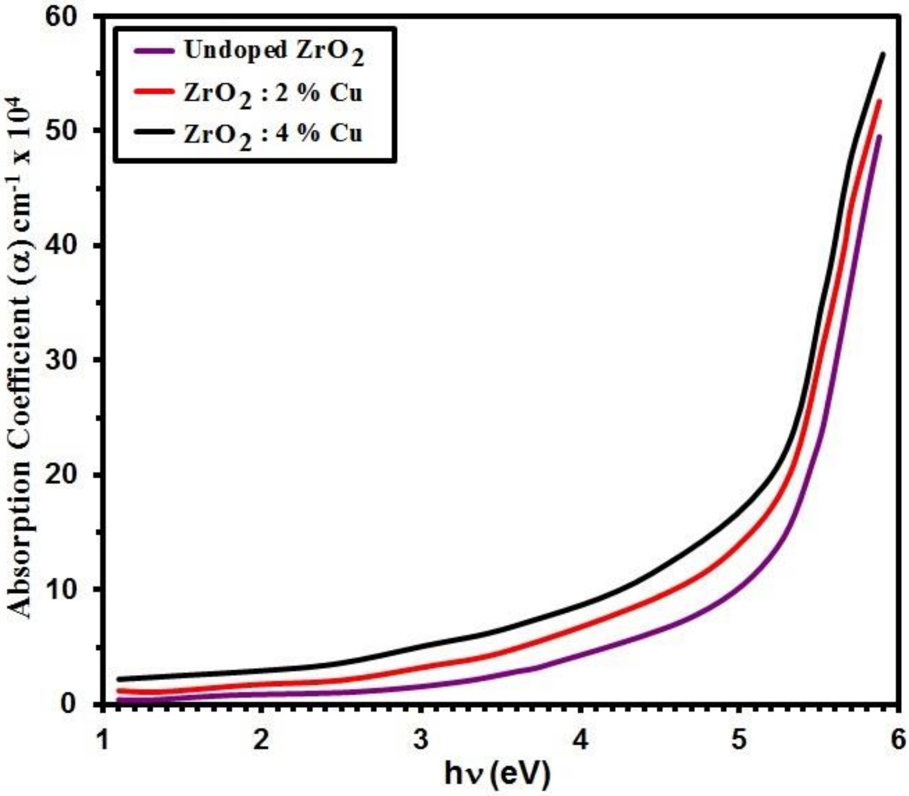

Fig. 5. α Vs. hν for intended films.

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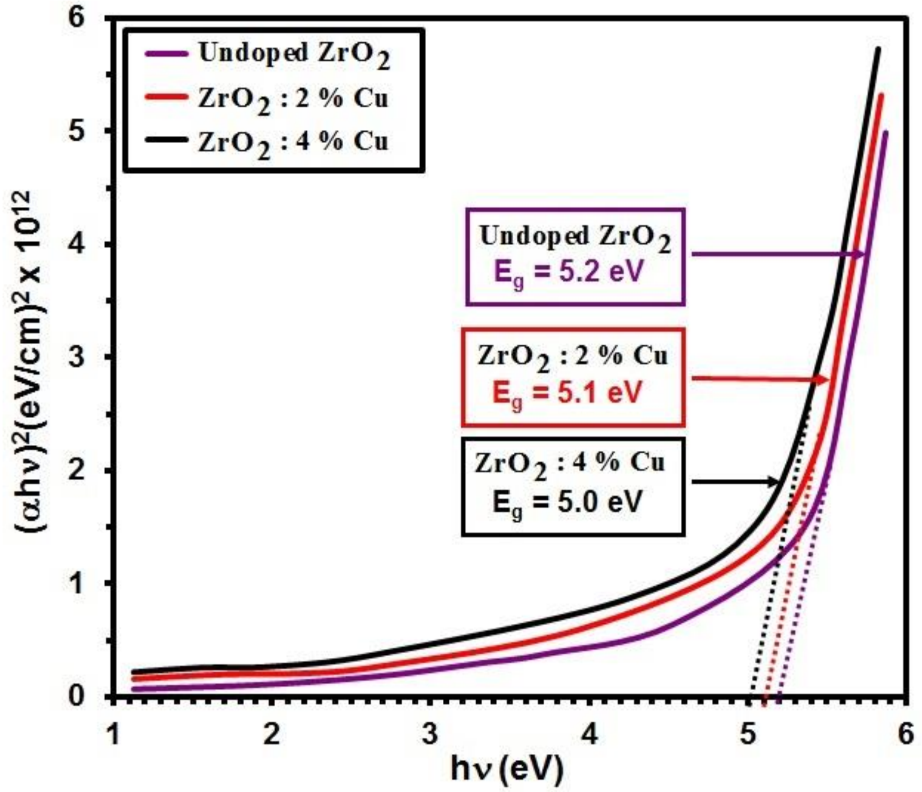

Fig. 6. $(\alpha h\nu)^2$ Vs. hν of intended films.

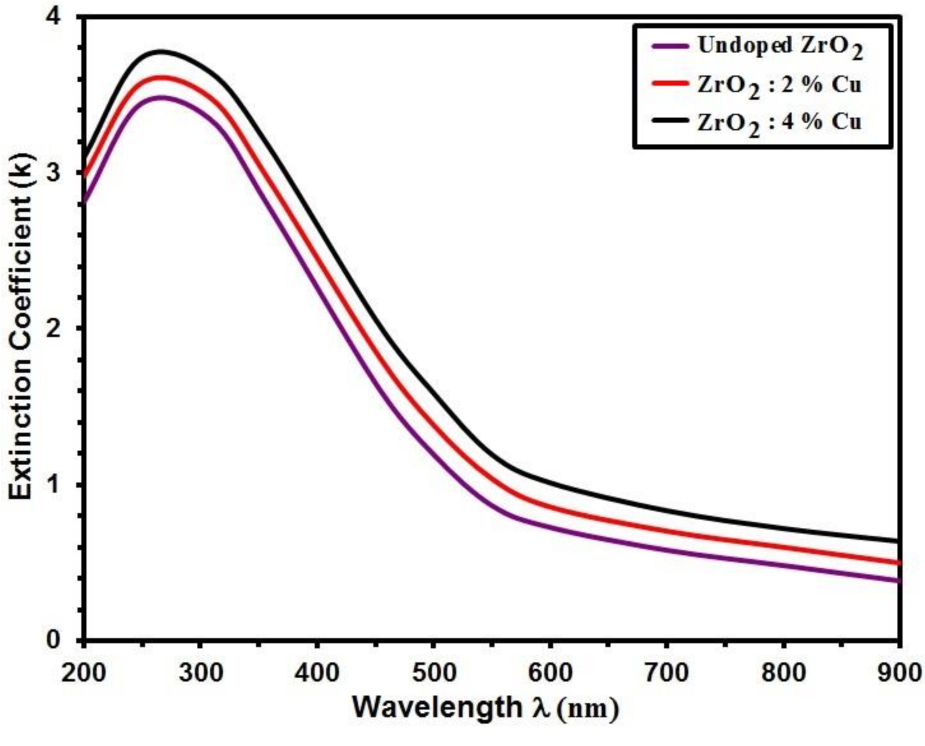

Fig. 7. Extinction coefficient (k) of the grown films.

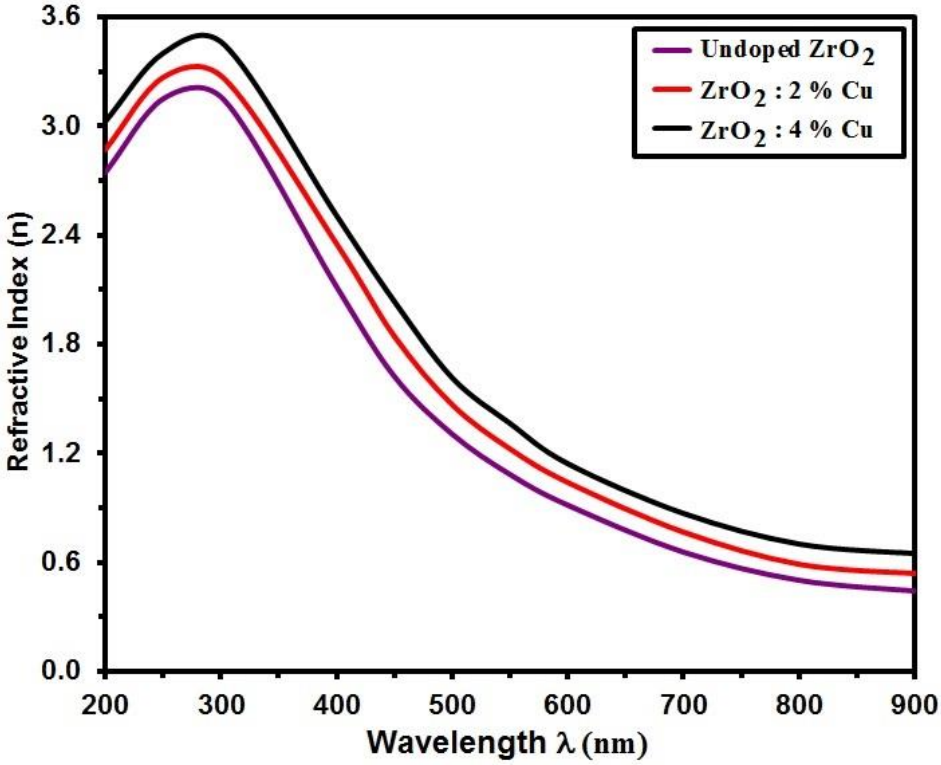

Fig. 8. n for grown films

Eq. 5 : [41–43] can be used to calculate the bandgap Eg:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^{\frac{1}{2}} \quad (5)$$

Fig. 5 illustrates that A is the constant. The energy gaps values are displayed in Fig. 6, where they are shown to drop from 5.2 eV for an undoped ZrO_2 thin film to 5.0 eV over 5% Cu-doping.

(α) and the extinction coefficient can be related by [44,45]:

$$K(\lambda) = \frac{\alpha(\lambda)\lambda}{4\pi} \quad (6)$$

Where k (λ) is extinction coefficient.

The extinction coefficient related inversely with wavelength for all deposited nanostructured Cu-doped ZrO_2 thin films as in (Fig. 6.) In addition, increasing Extinction coefficient when increasing Cu-doping in the ZrO_2 thin films.

Fig. 7. Illustrate the relation between k(λ) , which offer a decrement of its value with increment of Au until 550 nm, thereafter no change of k(λ).

The refractive index (n) was obtained via the relation [46, 47]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (7)$$

Fig. 8. shows refractive index against wavelength for (Cu-doped) ZrO_2 thin films showing a decrease of n with increasing (Cu) content

CONCLUSION

Nanostructured zirconium oxide is grown by spray pyrolysis method. XRD displayed that zirconium oxide films have (200) dominant peak. *[D]* increases from (15.990 -19.780 nm) as Copper content, whilst strain (ε) decreased from 2.160 - 1.750 , whilst dislocation density (δ) decreased from 3.91 - 2.55. The AFM have revealed that the The crystallite size, roughness average and rms were lawering with the high Cu-doping respectively, The increase in Cu-doping drives to a decrement in transmission values, whilist adecrease in band gap from 5.2 eV to 5.0 eV is seen. the absorption coefficient ,refractive index and extinction coefficient were also determind.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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