Aluminum doping Nanostructured CuO Thin films to enhancement some physical properties

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Abstract

CuO and CuO: Al thin films were precipitation on glass base at 400°C utilizing chemical spray pyrolysis (CSP) technique. XRD test disclosed that all films are polycrystalline with predominant peak at (111). AFM analysis displayed the surface topography of Undoped and Aluminum doped CuO thin films are nanostructure. Optical characterization shows all the films are highly transparent in visible area. A shift from E_g = 1.97 eV to 1.87 eV is seen when increasing doping in Al. The refractive index is affected via Aluminum content.

Keywords: CuO: Al thin films, CSP, XRD, AFM and Optical properties.

تحسين بعض الخصائص الفيزيائية لأغشية اوكسيد النحاس ذات التراكيب النانوية باستخدام التشويب بالألمنيوم

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الملخص

حضرت اغشية اوكسيد النحاس النقية والمشوبة بالألمنيوم المرسبة على القواعد الزجاجية عند درجة حرارة ٤٠٠ مئوي باستخدام طريقة الترسيب الكيميائي الحراري. فحوصات الخصائص التركيبية بينت ان كل الأفلام المحضرة هي متعددة الاتجاهية والاتجاه الأقوى هو (111)

فحوصات جهاز AFM اظهرت ان جميع الأفلام المحضرة ذات تركيب نانوي. الخصائص البصرية اظهرت ان جميع الأفلام ذات نفاذية عالية. كذلك هناك تغير في فجوة الطاقة من 1.97 eV الى 1.87 eV مع زيادة التشويب بالألمنيوم. كذلك معامل الانكسار n يعتمد على تركيز مادة الالمنيوم المشوبة.

الكلمات المفتاحية: أغشية CuO: Al، الرش الكيميائي الحراري، XRD، AFM، الخصائص البصرية.

Introduction

Progress metal chalcogenides are completely considered due to their favored physical and synthetic properties over the most recent couple of many years. Among these considerations are those about Copper oxide that is a critical p-type semiconductor [1-3]. In the latest couple of years, Nanostructures materials are found considering as they have exceptional qualities which are not viably gotten from common noticeable perceptible materials. The intricate crystal chemistry of Copper oxide was expected in view of its steadiness that engages it to outline stoichiometric mixes. Copper oxide was seen as engaging materials because of the wide collection of mechanical applications they have including, for instance, ferroelectric slight movies, high-thickness optical data storing [4] optoelectronic devices [5], energy accumulating and change [6], daylight based cells, gas sensors [7], on account of their essential, optical and electrical properties [8]. Copper oxide shows high transmission near IR district of (800 – 1500 nm) [9]. It was deposited by a number of techniques including spray pyrolysis [10], sol–gel synthesis [11] and electrodeposition [12, 13], sol-gel synthesis [14], CVD [15], PLD [16]. The current study is about the grown of CuO and CuO: Al thin films by chemical spray pyrolysis. It likewise foe CuO on the effect on basic and optical properties it has including absorption coefficient (α), transmittance (T), and the films bandgap energy. Using AFM, the film surface morphology was talked about. Using XRD, the auxiliary portrayal was additionally contemplated.

Experiment

CuO thin films were grown by CSP technique, using $CuCl_2$ (purity: 99.99%) from Sigma-Aldrich The volumetric ratio of Aluminum chloride dopant was 2% and 4%. (purity: 99.98%) from Merck Germany. The solutions were sprayed on glass bases with filtered air kept at a pressure of 10^5 Pa. The flow rate is 5 ml/min and deposition time 8 sec followed by 2 minutes wait to prevent extravagant cooling. The base temperature was 400 ^oC. The space from spout to the base was 28 cm. Film thickness was calculated via gravimetric method, their values were 340 ± 30 nm. Optical transmittance was calculated employing UV-VIS spectrophotometer. XRD and AFM were employed to obtain films structure and morphology.

Results and Discussions

The X- ray diffraction of Undoped CuO and CuO: Al films appear in Figure (1). It is seen that places of XRD pinnacles of grown films film are set at points ($2\theta\sim$ 35.34^o, 38.72^o, 53.45^o and 62.21^o) in correspondence to the planes (111), (200), (020) and (311) separately that are remembered for the hexagonal structure with orientation of (103). These peaks agree with (ICDD) card number (041-0254). Scherrer's formula could figure the readied thin films crystallite size (D) by the equation underneath, as follows [17]:

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

Where λ is X-ray wavelength, β represents (FWHM) and θ is Bragg's angle. Table 1 offers the values of D were (11.40 nm) and (12.62 nm) for Undoped CuO and CuO:3% Al thin films, individually. The expansion in response doping Aluminum brings about grain development accordingly an increment in crystallite size, though the strain (%) parameter diminishes from 24.94 to 22.03. The following equation [18] was utilized to assess the dislocation density (δ) in the thin Films.

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

The following equation [19] was utilized to assess the strain (ε) in the thin Films.

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

The values of *D* are shown in Table 1.

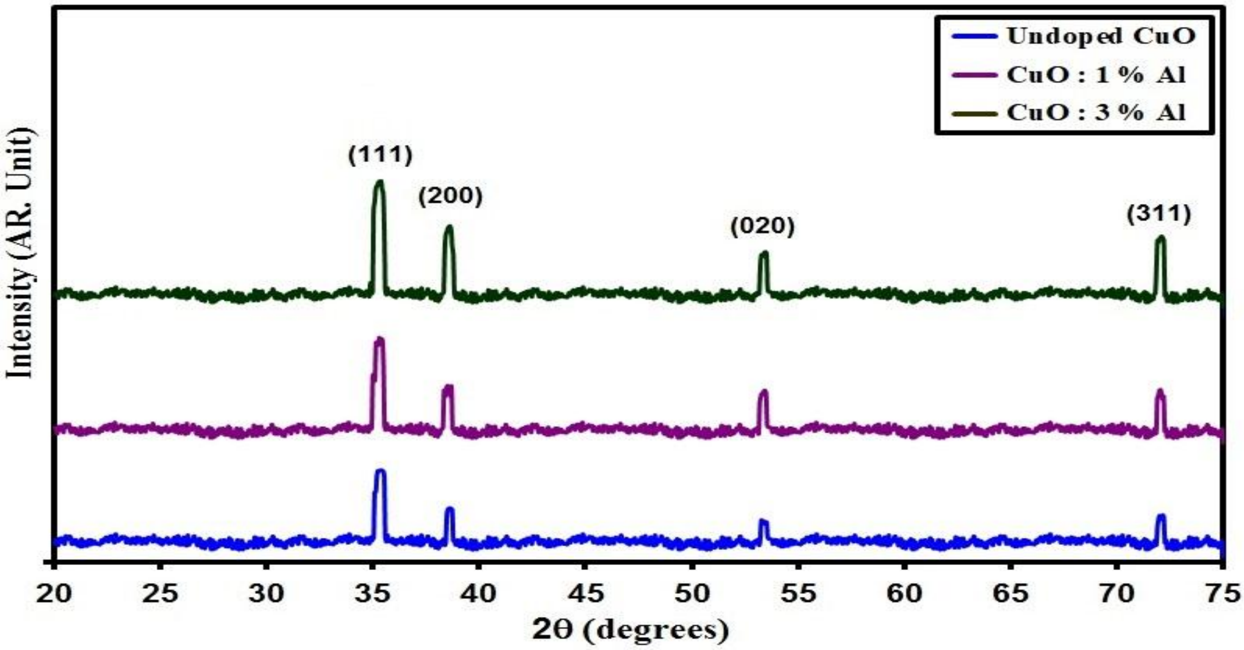

Fig.1. XRD styles of the intended films.

Table 1. D, E_g and structural parameters.

Samples	2 θ (°)	(hkl) Plane	FWHM (°)	Optical bandgap (eV)	Grain size (nm)	Dislocations density ($\times 10^{14}$)(lines/m^2)	Strain ($\times 10^{-4}$)
Undoped CuO	35.33	111	0.60	1.97	13.90	51.75	24.94
CuO: 1% Al	35.34	111	0.57	1.92	14.63	46.72	23.36
CuO: 3% Al	35.34	111	0.53	1.87	15.73	40.41	22.03

The FWHM, D, δ and Strain as a function to the prepared films are represented in Figure (2). It also shows the inverse connection between the size of the crystalite and other parameters. Figure (2) demonstrates β, D, δ and ε Strain via doping.

Table 2. P_{AFM} of the intended films.

Specimen	Average Diameter nm	R_a (nm)	R_{rms} (nm)
Undoped CuO	57.09	5.78	4.83
CuO: 1% Al	50.73	4.29	3.46
CuO :3% Al	43.21	3.25	2.26

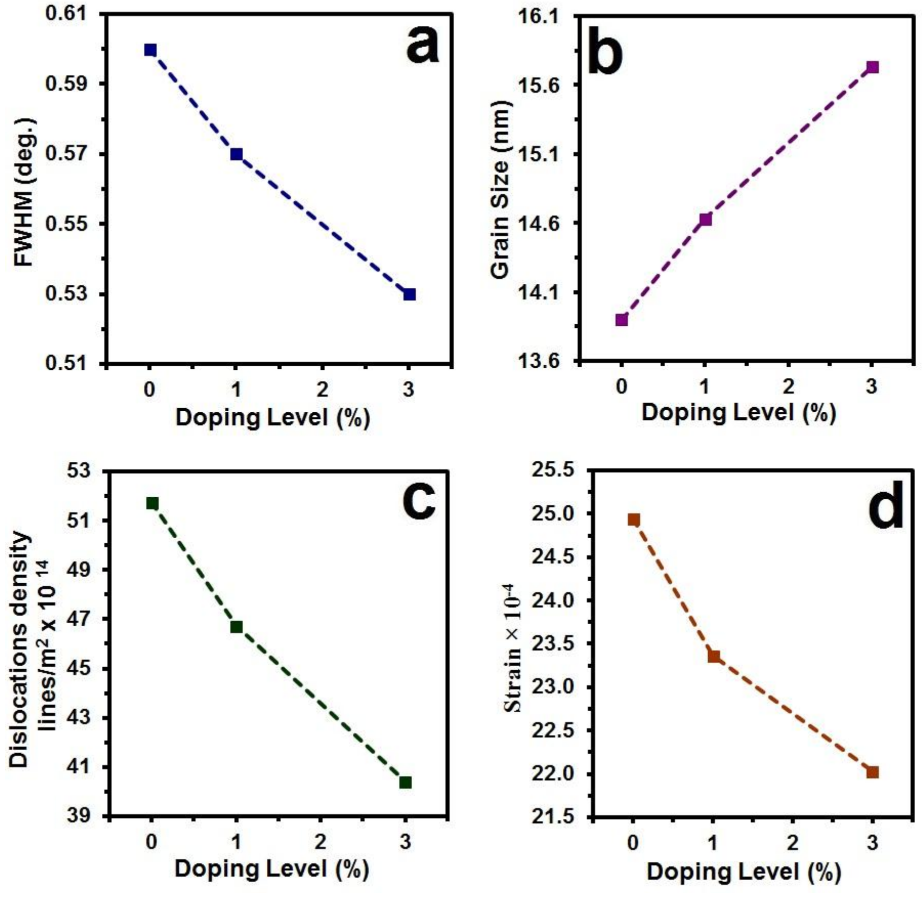

Fig. 2. FWHM (a) D (b) δ (c) ε (d).

For the grown films, an (AFM) was applied. 3D AFM image of Undoped CuO thin films are displayed in Figure 3 (a_1, b_2 and c_1). CuO thin films has larger grain size indicating high crystallinity and good surface morphology. The root mean square roughness (R_{rms}) and average roughness (R_a) are offered in Table 1. The R_{rms} and R_a follow the doping. The diameter size is noted to be (57.09), (50.73) and (43.21) nm for CuO films grown at CuO: 1% Al and CuO: 3% Al, respectively, The R_{rms} value of 4.83 nm for grown CuO film, thin films decreased to 2.26 nm by decreased CuO: 3% Al, R_a roughness parameters as a function of dopant concentration were given in Fig. 3 (a_3, b_3, and c_3) respectively. Table (2) show the AFM parameters P_{AFM}.

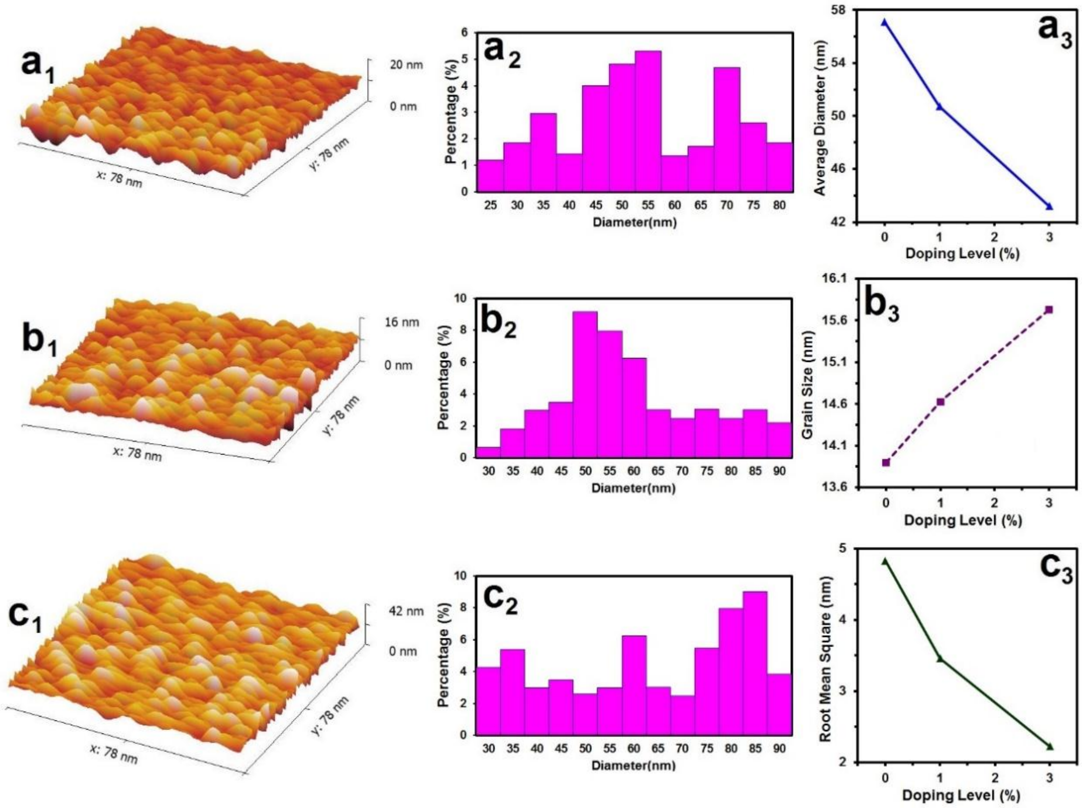

Fig.3. AFM images (a_1, b_1 and c_1), granularly distributed (a_2, b_2 and c_2) and Variance of P_{AFM} via doping (a_3, b_3 and c_3).

Figure 4 offers transmittance (T) via wavelength. CuO film is transparent in Vis region with about 69 %, indicating good transparency. T decreases as Aluminum increases, which might be due to lattice defects [20].

The absorption coefficient (α) could be calculated employing the following relation [21]:

$$\alpha = (2.303\times A)/t \qquad (4)$$

Where (t) stands for film thickness. Figure (5) demonstrates the relationship between the α versus photon energy. From Figure (5), we can conclude that α of Undoped CuO thin films relayed on the Aluminum-content and E_g increase as Aluminum increases.

The bandgap of the Undoped CuO and CuO:Al films can be calculated using Tauc's relation [22]:

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \qquad (5)$$

where hν is the photon energy, A is a constant, the plot of $(\alpha h\nu)^2$ versus (hν), is displays in Fig.6. the bandgap of CuO thin films depends on the Aluminum content and E_g decreases as Aluminum increase. The bandgap values of the synthesized nanocrystalline Undoped CuO and CuO:3% Al thin films are 1.97 and 1.87 eV, respectively. Table (1) illustrate the values of bandgap.

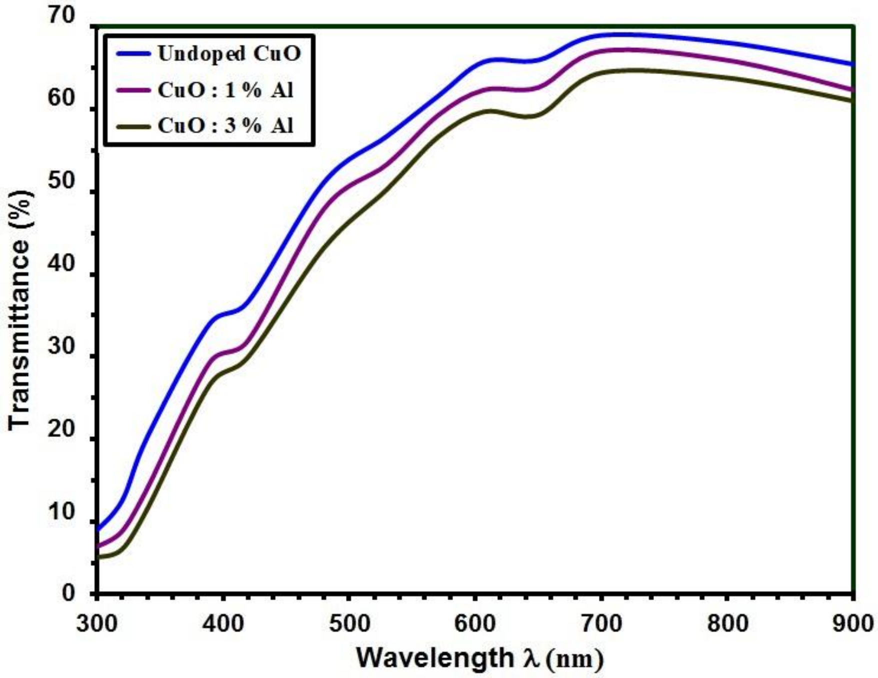

Fig.4. Transmittance of intended films.

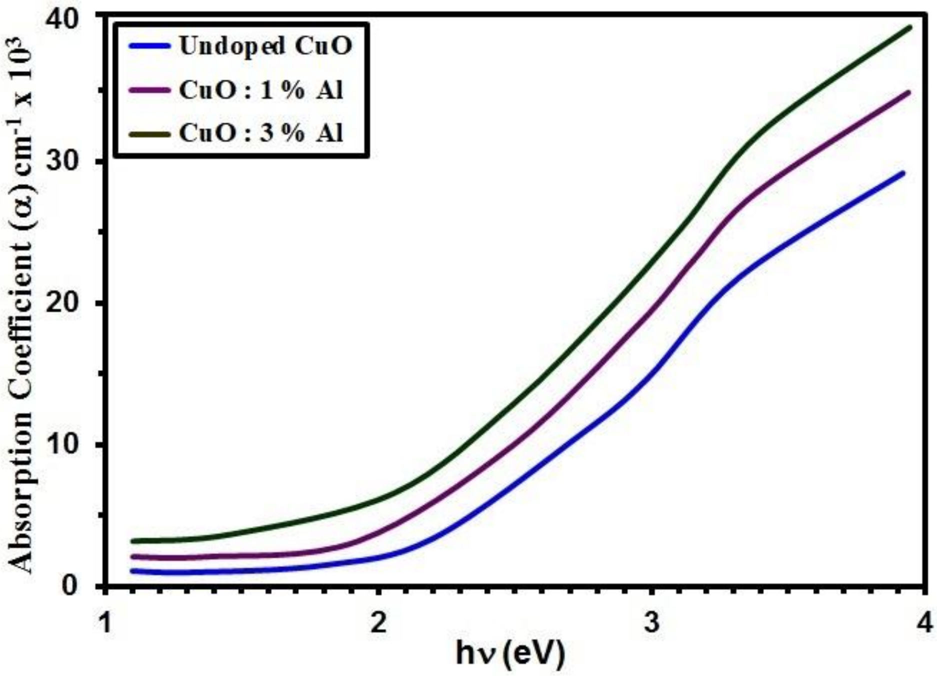

Fig. 5 α Vs hν of the intended films.

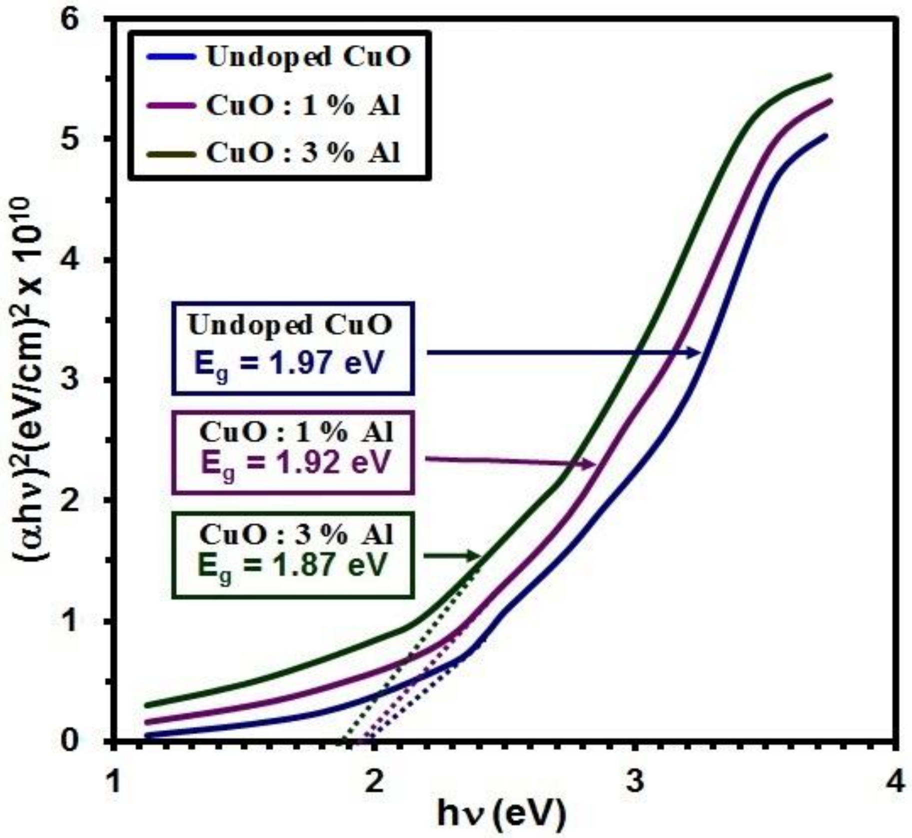

Fig. 6. $(\alpha h\nu)^2$ Vs hν of the intended films.

refractive index (n) and the extinction coefficient (k) can obtained by these relations [23]:

$$n = [1 + R/1 - R] + [4R / (1-R)^2 - k^2]^{1/2} \quad (6)$$

$$k = \alpha\lambda/4\pi \quad (7)$$

Where λ is the wavelength. n was calculated by using Eq. (6) and the variation of n is shown in Fig. 7. There is a small decrease in n for Aluminum doping. values of n are varied between (3.86–3.64) at long wavelengths. The lowering of n can be assigned to the density and the surface roughness [31]. Fig. 8. displays the variance k with wavelength for all films. It can be notice that there is slightly decrease in the extinction coefficient after Aluminum doping.

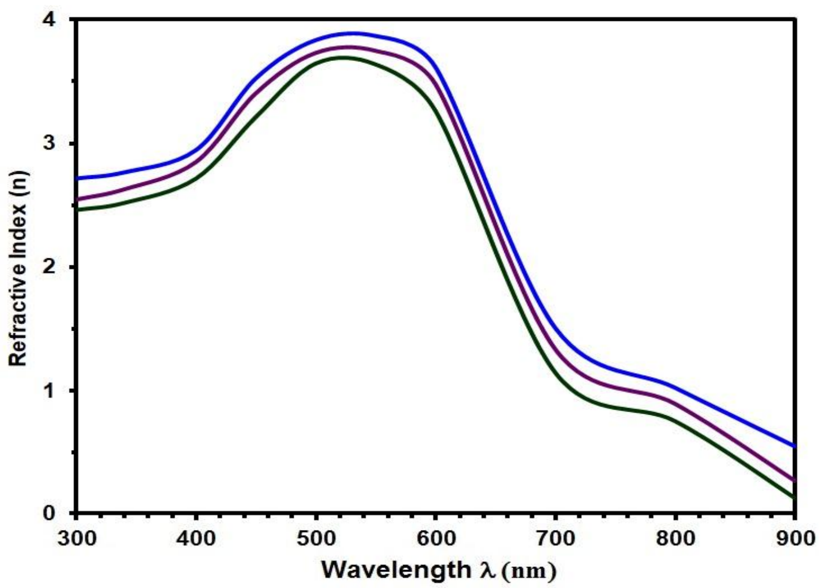

Fig. (7) n of the intended films.

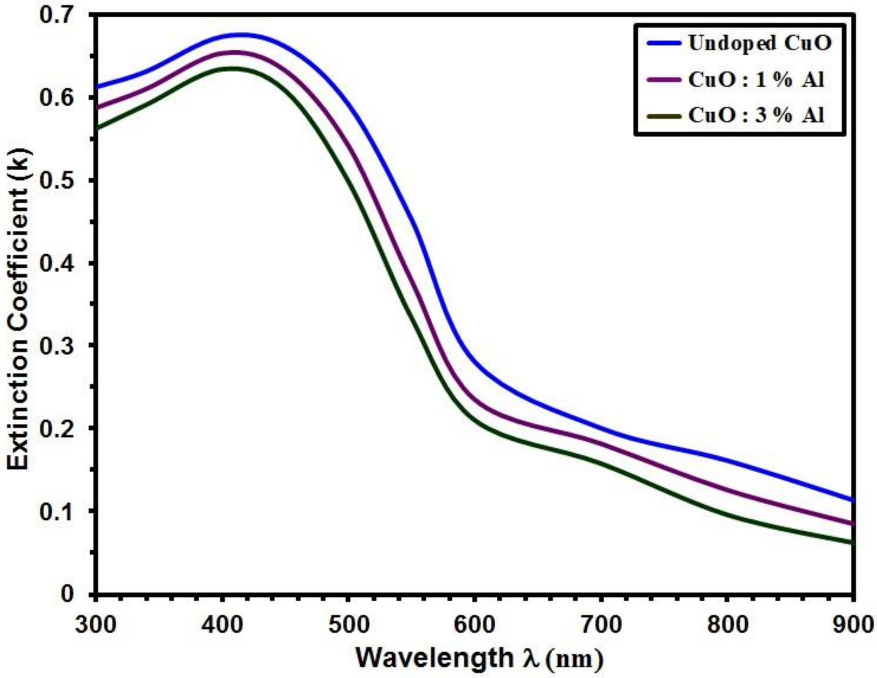

Fig. (8) k of the intended films.

Conclusion

An appropriate chemical spray pyrolysis (CSP) strategy was applied. Undoped CuO thin film on glass at various concentrations was deposited. The XRD that are gotten exhibited that the CuO film was polycrystalline notwithstanding covellite-hexagonal structure and favored direction along the plane of (111). The Grain size for pure CuO molecule is about (13.90-15.73) nm with CuO:3% Al, while the strain (%) boundary expanded from 24.94 to 22.03, Surface morphology study shows that higher grouping of Aluminum doped CuO thin film were of high caliber, The grain size of the nanoparticles saw in the scope of (57.09), (50.73) and (43.21) nm for the Undoped CuO, CuO:1% Al and CuO:3% Al separately, thin films of UV–VIS range information demonstrated that the aluminum fixation esteem will have its impact on the as-kept CuO thin films optical properties. It is concluded that the optical change diminishes from 69% - 65% in the vision range, when the concentration was expanded, and the optical band gap E_g decline with expanding Aluminum doping from (1.97 – 1.87) eV.

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