Journal University of Kerbala , Vol. 15 No.2 Scientific . 2017

Study the Effect of Copper (Cu) Doping on the Structure Properties of Zinc Oxide (ZnO) Prepared by Using Pulsed Laser Deposition (PLD)

دراسة تأثير التشويب بالنحاس (Cu) على الخواص التركيبية لأوكسيد الخارصين (ZnO) المحضر بطريقة الترسيب بالليزر النبضي (PLD)

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Abstract

In this research the structural properties for pure zinc oxide (ZnO) thin films and ZnO doped with (6 and 9) % weight percentage of copper have been investigated. The thin films have prepared by using pulsed laser deposition (PLD) technique, they synthesized by using the following parameters; Nd:YAG laser (λ=1064 nm), repetition rate of (6 Hz), pulse duration of (10 ns), energy (100 mJ) and vacuum pressure (10^{-5} mbar). The thin films have deposited on glass substrate at (250^0C). The XRD shown the films were polycrystalline in hexagonal phase with peaks belong to cubic phase. The calculations from XRD data shown the crystallite size decreasing from (46.98-56.57) nm for pure zinc oxide to (34.70 and 44.49 nm) for copper doped ZnO with (6 and 9) % respectively, other structure parameters (bond length, dislocation density, lattice constants, strain) have been calculated. Investigated by AFM and SEM confirm that thin films have high homogeneity and the grains have rod-like structure. The EDX diagram didn't show any other phase which indicate that the doping substitution type because closeness between Zn and Cu atoms.

Key words: ZnO ,Nanoparticles, , PLD , Zinc Oxide doped with Cu , AFM, SEM.

الخلاصة

في هذا البحث تم دراسة الخواص التركيبية لأغشية اوكسيد الخارصين (ZnO) الرقيقة النقية والمشوبة بمادة النحاس(Cu) وبنسب وزنيه % (6 and 9) , الأغشية الرقيقة تم تحضيرها باستعمال تقنية الترسيب بالليزر (PLD),حيث تم تحضيرها باستخدام المعلمات التالية ليزرNd:YAG (λ=1064 nm) , معدل التردد (6 Hz), عرض نبضة (10 ns) وبطاقة (100 mJ) وتحت ضغط (10^{-5} mbar) . الأغشية الرقيقة تم ترسيبها على شرائح من الزجاج وعند درجة حرارة (250^0C) . بينت النتائج حيود الأشعة السينية (XRD) إن الأغشية ذات تركيب متعدد التبلور عند الطور السداسي مع ظهور بعض القمم تعود للطور المكعب. تؤكد الحسابات المستحصلة من قياسات XRD ان الحجم البلوري يتناقص من nm (46.98-56.57) لأغشية ZnO النقية الى 34.70 and 44.49 nm لأغشية ZnO المشوبة بمادة النحاس % (6 and 9) على التوالي كذالك تم حساب (طول الآصرة , كثافة الانخلاعات , ثوابت الشبيكة , المطاوعة) لأغشية المحضرة . أكدت الفحوصات باستخدام AFM و SEM بأن الأغشية الرقيقة المحضرة تكون متجانسة بشكل كبير وان حبيبات المكونة لها ذات تراكيب شبه قضيبية. أن المخططات EDX لم تظهر وجود طور جديد مما يؤكد حدوث عملية استبدال بين كل من ذرة Zn و Cu أثناء عملية التشويب.

الكلمات المفتاحية : ZnO, Nanoparticles, PLD , اوكسيد الخارصين مشوبة بالنحاس (Cu), AFM , SEM

1. Introduction

The invented first working LASER based on Ruby on May 16th 1960, from that time laser has been used as effective device play impotent role for a lot of scientific fields. One of these particularly application is in the materials processing technology [1]. Laser beam has certain unique characteristic, such as high monochromaticity, coherence (spatial & temporal), high brightness, and high energy density. If the laser beam has high enough power, material will melt and vaporize even for stiff and high heat resisted materials. Moreover attributed to excessive accuracy, high beam

quality, and easy integration with computer controlled (CNC) machines, lasers have numerous applications in the industry such as cutting, drilling, welding, materials modification and material surface treatment. There are also non-materials processing applications involving alignment, inspection and scanning. When high-power pulsed laser beam is focused inside chamber under vacuum or background gas to strike a target of the material that can be ablated and deposited onto different substrates to create high quality thin films. This technique of laser application is so-called pulsed laser deposition (PLD) [2-5].

In pulsed laser deposition, high pulsed laser beam is usually focused onto the surface of the target. If the absorption for laser radiation by the surface of target strong enough rapidly evaporation of the target materials will occur. The evaporated materials from target surface usually include highly excited and ionized species. They demonstrated themselves as glow plasma plume which expands along the direction normal to the target surface if the ablation occurs in vacuum. The interaction between laser ablation plume and a background gas is very important in PLD process, nanoparticles formation, and growth will be affected clearly [6]. Differently from expansion into a vacuum, the interaction of the plume with background gas is a far more complex gas dynamic process attributed to the existence of new physical processes such as deceleration, recombination, forming of shock waves, interpenetration, and aggregation [7,8]. Optimum characteristic of thin films were deposited by PLD technique require the use of a suitable gas to achieve high-quality films, for good conductivity and demanding transparency [9,10].

2. Experimental Method

In this study, preparation technique of series of $Cu_xZn_{1-x}O$ thin films are (x=0 , 0.04, 0.06 , 0.07, 0.09) where the characterization techniques are described.

Special aspects of experimental strategies are also pointed out and elaborated wherever necessary**.** To preparation nanoparticles thin films, we used the PLD system it consist of main parts shows in figure (1). vacuum chamber, Q- switched Nd:YAG Laser**,** lens with focal length (30)cm**,** Quartz window, pressure monitoring**,** rotary pump, diffusion pump and Ar gas bottle. To preparation nanoparticles thin films used the following steps:

1- Cleaned the vacuum chamber by acetone**.**
2- Put glass Slides on a slides holder so that it is against the target on the rotated target holder and the distance between the target surface and the Slides 3 cm.
3- The Nd:YAG Laser radiation is focused by lens with focal length 30 cm on the surface of a rotated target at the incident angle of approximately 45°.
4- closed the vacuum chamber, close all valves and started the process of creates a vacuum , initially rotary vane pump which creates a vacuum of ~10^{-3} mbar ,diffusion pump becomes operational and can create a vacuum up to ~10^{-6} mbar**.**
5- The substrate heated to (250^{o}C) by using Halogen lamp to improve the adhesion of deposited material**.**
6- After reaching the desired vacuum, vacuum chamber valve open and give laser pulses plasma column consists that contains nanoparticles which are deposited on the slide.

Fig.(1) PLD system Set-Up

The structural properties of thin films were analyzed and calculated from XRD data with Cu Kα (λ=1.5406A°) by using (XR – DIFRACTOMETER / 6000) , Shimadzu. The surface morphology of thin films have been investigated by SEM and AFM (AC-AFM, PicoLE, Molecular Imaging) at Ferdowsi university of mashhad (Iran).

3-Results and Discussion

3.1 XRD Analysis

To calculate constructively the spacing (d) between diffracting planes in a few specific directions, determined by Bragg's law [11]:

$2d\sin\theta = m\lambda$ ……. (1)

Where θ is the Bragg angle, m is any integer, and λ is the wavelength of the beam of X-Ray, λ=0.15406 nm. These specific directions shows as spots on the diffraction pattern called reflections. The lattice constants (a and c) can be found from the equations [8]:

$$\left.\begin{aligned} a &= \lambda/3\sin\theta \\ c &= \lambda/\sin\theta \end{aligned}\right\} \quad \text{----------(2)}$$

The crystallite size (*Gs*) of particles, or crystallites can be determined by using Scherer equation [12]:

$$G_s = \frac{0.89\lambda}{\beta\cos\theta_B} \quad \text{……. (3)}$$

where 0.89 is the shape factor, denoting the ratio of a particle's major dimension to its minor dimension , λ is the X-ray wavelength, β is the full width at half maximum (FWHM) of intensity in radians, and θ is the Bragg angle; G is the crystallite size.
The strain (ε) can be calculated by using the relation [13]

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \quad \text{……. (4)}$$

The dislocation density (δ) known as the length of dislocation lines to crystal size (considered as the value of defect in samples) can be found by using the relation [14]

$$\delta = 1/ G^2_s \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

Figure (2) shown the X-ray diffraction of zinc oxide thin films prepared with laser energy (100mJ) and at wavelength 1064 nm, the films were polycrystalline in hexagonal phase, notice appearing new peaks of cubic phase represent with plane (101)and angle 43.9^0 as compared wit h standard value. And have the same thickness at room temperature, the result of x-ray diffraction shown the peak position with miller indices(002),(100),(110),(101) and (102)with crystallite size value between (46.98-56.57)nm and there where shifting in peaks position , the highest value where for plane(002) and its lattice constant (a and c)where close to the standard values. The crystallite size was measured by using Scherer equation. The parameter of x-ray diffraction such crystallite size, intensity bond length, dislocation density, and other shown in table (1) of (002) plane.

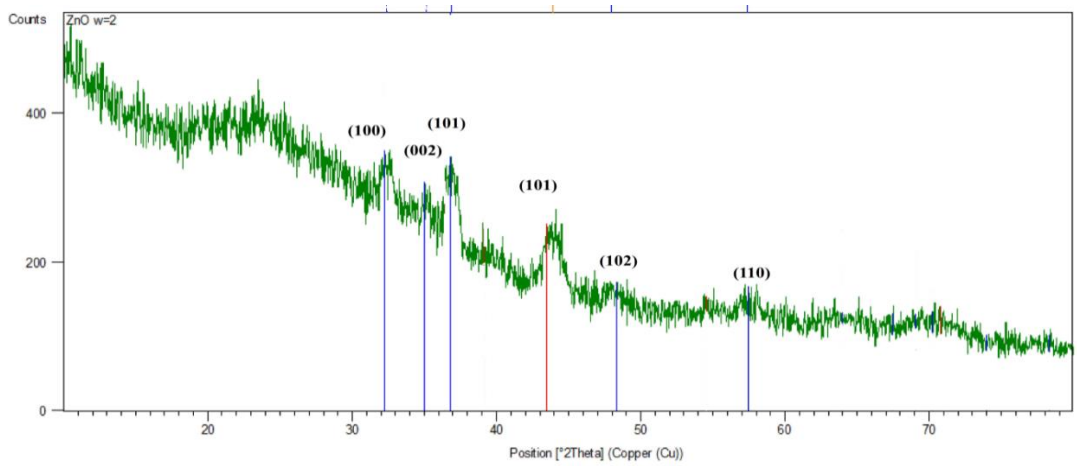

Fig. (2) X-ray diifraction of pure ZnO thin films

Figures (3) and (4) shown the x-ray diffraction of ZnO doped Cu with weight percentage (6 and 9)% respectively with laser energy (100 mJ) at wavelength (1064 nm) , the figures have shown that after doping the intensity of peaks decreased lead to decreased the intensity of plane (002) the decreased in the height of peaks indicates a low crystalline in the films and increased crystal defect, the crystallite size that calculated by using equation (3) decreased after doping to (34.70 and 44.49 nm) for (6 and 9) % respectively ,as shown in table (1) and other parameter of x-ray diffraction such as intensity bond length , dislocation density and other of (002) pattern. This is mainly because of the nucleation and subsequent growth rate with increasing Cu concentration which attributed to the difference between ionic radius of zinc and copper ions [15].

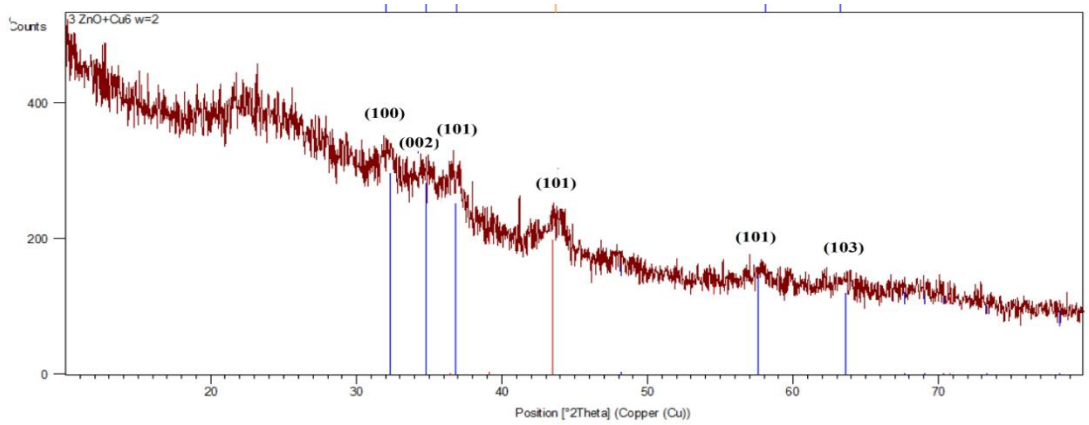

Fig. (3) X-ray diifraction of ZnO thin films doped with Cu (6%)

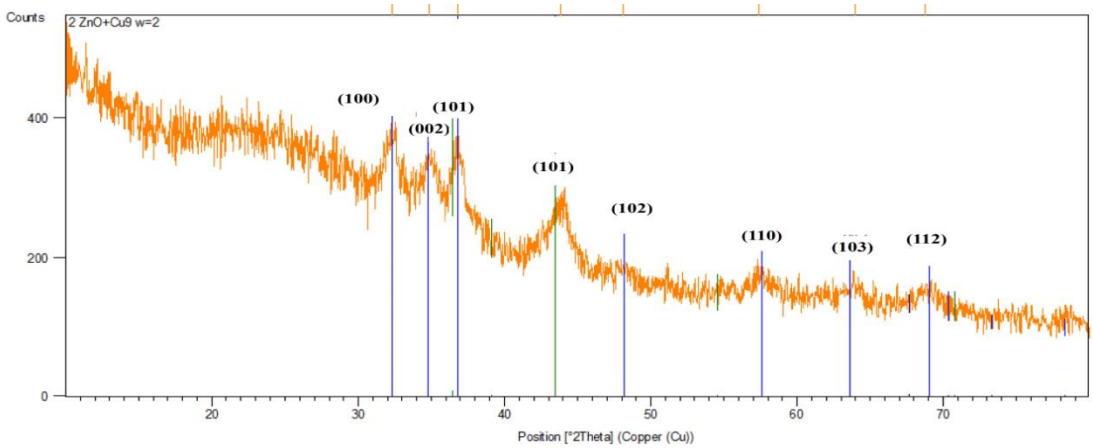

Fig. (4) X-ray diffraction of ZnO thin films doped with Cu (9%)

Table 1. The structural parameters calculated from XRD for pure & doped ZnO thin films

Sample	2θ	d(A°)	β(rad)	hkl	G.s(nm)	I	ε	a(A°)	c(A°)	δ(nm)$^{-2}$	L(A°)
ZnO	35.15	2.5509	0.15	002	56	400	0.0355	2.8289	4.8998	0.0334	1.5435
ZnO+Cu %6	34.8	2.5793	0.21	002	39.9	350	0.0501	2.9758	5.1543	0.0635	1.7288
ZnO+Cu %9	34.89	2.5695	0.18	002	46.66	390	0.0429	2.9684	5.1414	0.0465	1.7192

3.2 AFM & SEM Analysis

The results of topography surface shown in Figure (5) of ZnO thin films by using atom force microscopy (AFM) on glasses substrate prepared with laser energy (100mJ) ,wavelength (1064 nm) , and (250 °C)temperature notice that the grains at film surface have a high homogeneity with mean grain size (86 nm).

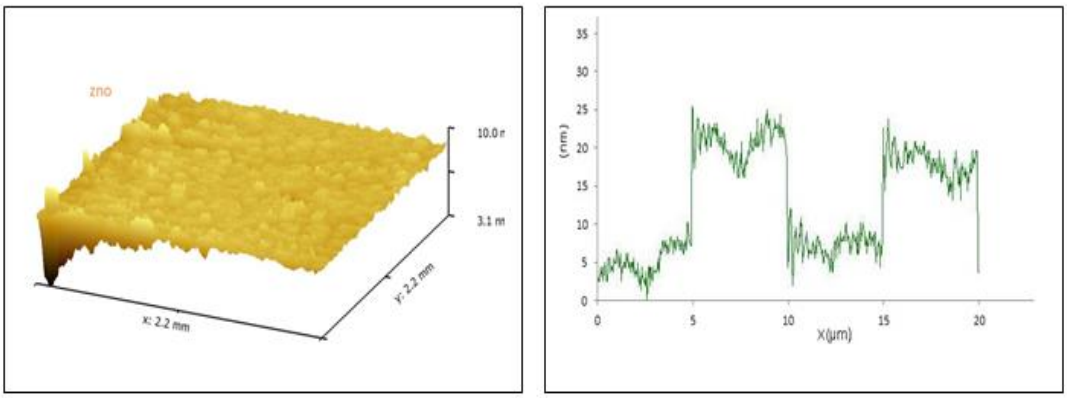

Fig. (5) AFM of pure ZnO thin films

After doping Cu with weight percentage (6 and 9)% notice that from surface topography of the film when doping with 6% the grain have a high homogeneity with mean grain size (80.96nm) , while at 9% the mean grain size where (53.51 nm) , and notice that the mean grain size decreased when the doping increased due to nucleation and subsequent growth rate with increasing Copper concentrations[15] as shown in figures (6) and (7).

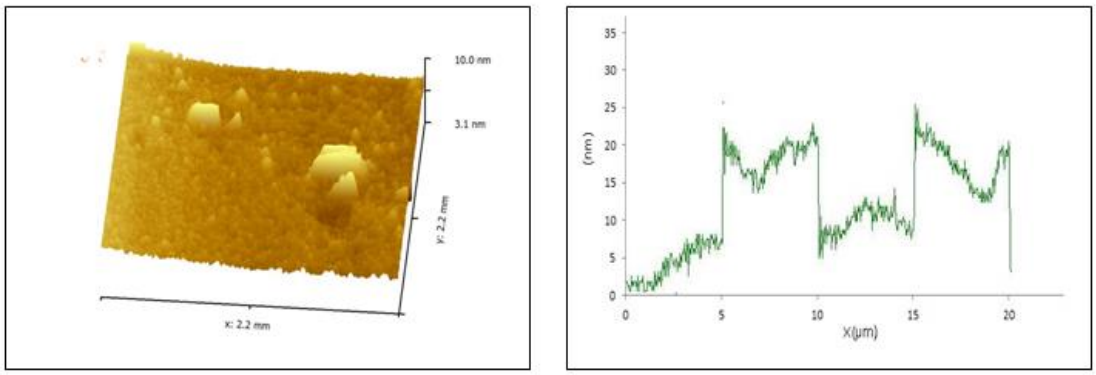

Fig. (6) AFM of ZnO thin films doped with Cu (6%)

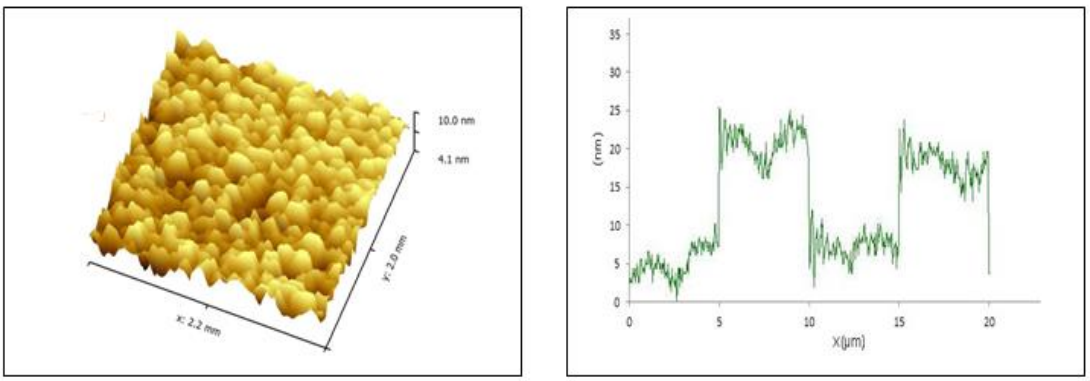

Fig. (7) AFM of ZnO thin films doped with Cu (9%)

The topography surface of ZnO thin film was examined by using scanning electron microscopy (SEM) from the image in figure (8) one can noticed that the nano grains have a good homogeneity with some vacancy between the grain in the high layer with presence some height appeared in white color , where the shape of particle determines by the laser incident angle, and according to its height and low from the surface, from the figure resulted that the grains have rod-like structure

.where it in grain growth stage , prefer in the vertical on base direct that indicate to c-axis ,the diameter value(31-22 nm) , which proved grown of wurtzite structure, While EDX diagram shown the presence of ZnO .

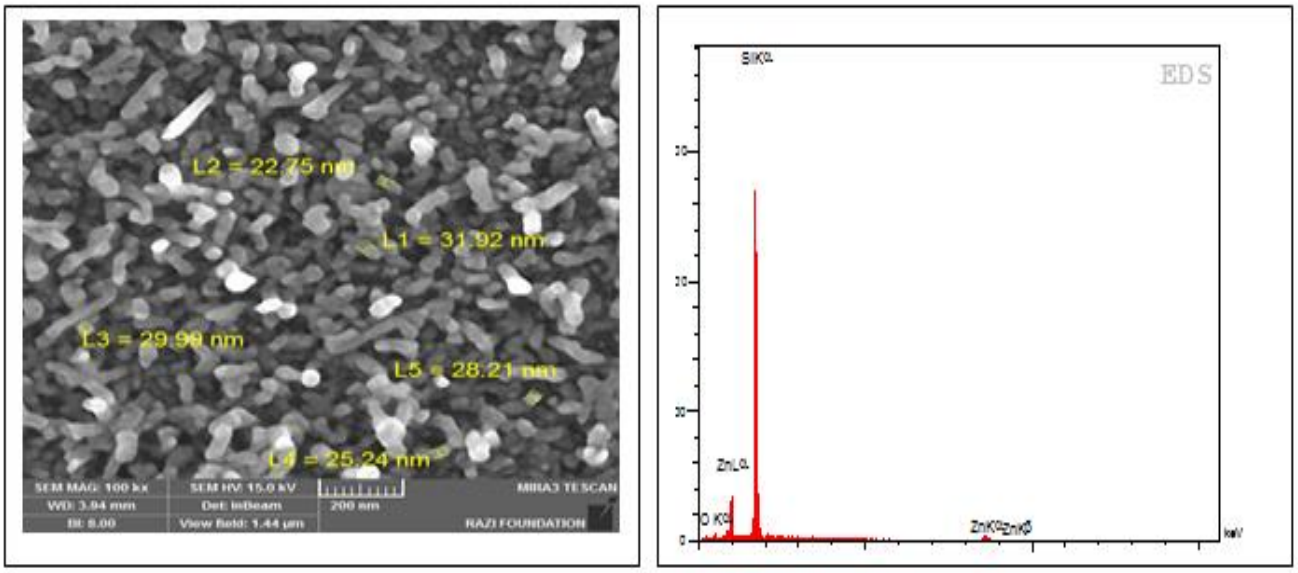

Fig. (8) SEM of pure ZnO thin films

The topography surface of ZnO doping with Cu shown in figures (9) and (10) which illustrated the image of scanning electron microscopic , noticed from the results that the film where highly homogeneity with presence of large spherical at doping rate 6% with low percentage , while when doping with 9% the particles more packing with appearing some large particles resulted from fusion between the small grain (coalescences) , also notice that the grain size decreased when the doping rate increased because increased neutral center . The EDX diagram didn't show any other phase which indicate that the doping substitution type because closeness between Zn and Cu atom.

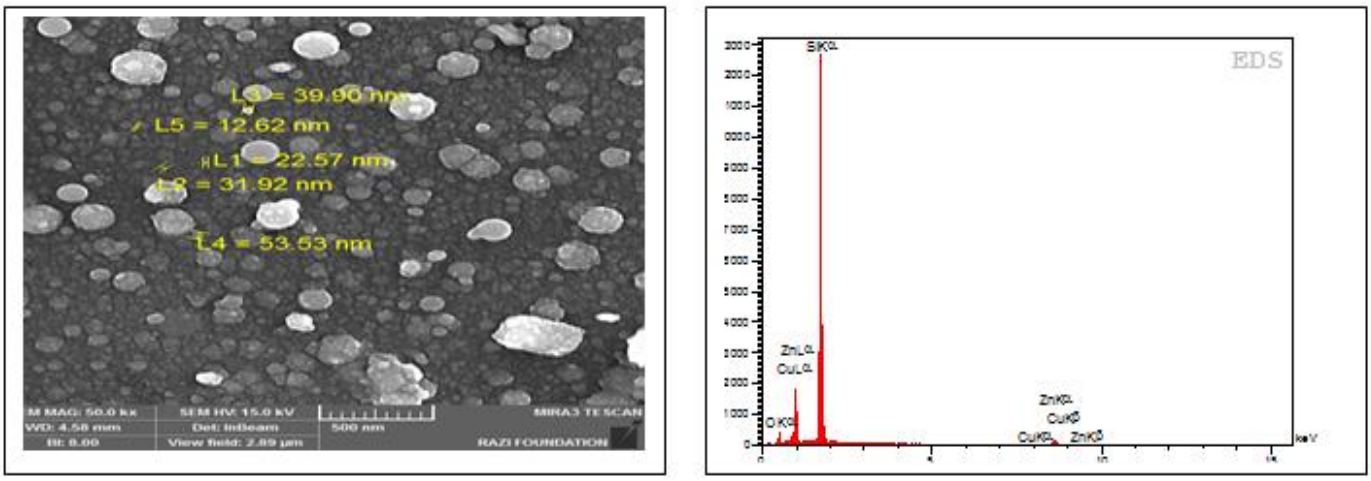

Fig. (9) SEM of ZnO thin films doped with Cu (6%)

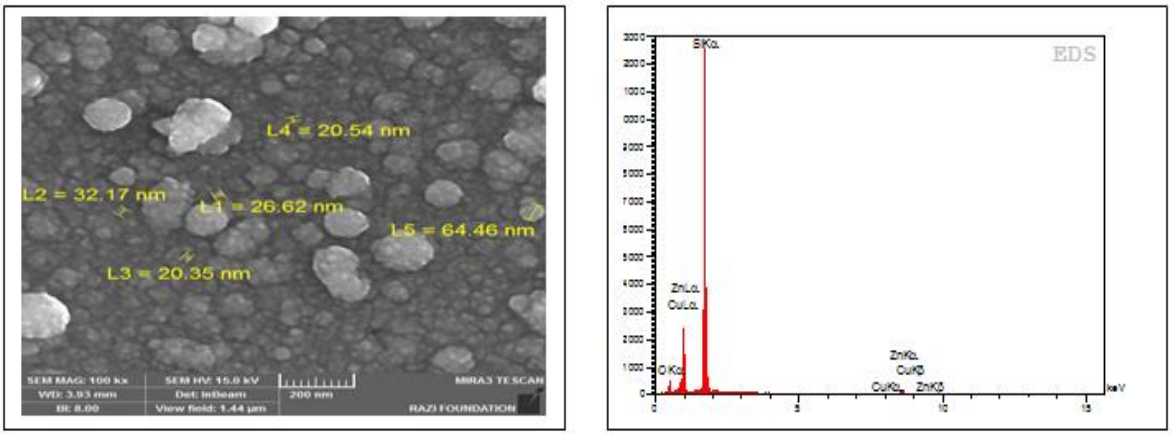

Fig. (10) SEM of ZnO thin films doped with Cu (9%)

4. Conclusions

In this study we have reported the synthesis of pure zinc oxide thin films and doped with (6 and 9) % weight percentage of copper by using pulsed laser deposition (PLD) on glass substrate, the X-ray diffraction shown that pure ZnO thin films were polycrystalline in hexagonal phase with evidence of cubic phase. After doping with copper the calculations from XRD data shown that there is decreasing in crystallite size while there is increasing in crystal defect of the thin films. The XRD calculations also shown there is increasing in bond length, dislocation density, lattice constants (a & c) and strain for ZnO doping with Cu compare with pure ZnO thin films. The analysis of topography surface of thin films by AFM and SEM confirm these results.

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