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To cite this article: Rashid Hashim Jabbar *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **571** 012109

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Study of Physical Properties and Sensitivity of Mercury Doped ZnO Thin Films

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Abstract:

Mercury doped zinc oxide (ZnO:Hg) thin films deposited on glass substrate at 400 °C, prepared by Chemical Spray Pyrolysis (CSP) technique for (3,6, and 9)% doping concentrations, structural properties has been measured by X-Ray Diffraction (XRD) which reveals the structure of (ZnO:Hg) thin films have been found the hexagonal wurtzite structure, crystallite size increases for ZnO:Hg(3%) then decreases with the increase of doping concentration. Atomic Force Microscope (AFM) used to measure granularity distribution, roughness and grain size. Increase of mercury doping leads to increasing of sensitivity for CO₂ gas.

Keywords: ZnO:Hg, CO₂, Gas Sensing, mercury doped.

Introduction:

Zinc oxide (ZnO) as a Transparence Conductance Oxide (TCO) have an excellence characteristics such as richness in nature, nontoxicity material, stable with band gap approximately 3.3 eV [1]. ZnO properties can be more important and improvement by adding doping materials [2]. This properties enable ZnO for using in several devices such as light emitting diodes, photodetectors, sensors, etc. ZnO is a significant material for an optical devices due to the high exciton binding energy which equal (60 meV) [3].

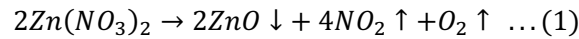
These remarkable features makes ZnO have good semiconductor material for several electronics devices as in light emitting diodes (LED), gas sensors, and field emitters, in the last years. ZnO can be prepared by using several techniques such as sputtering, chemical spray pyrolysis, chemical vapor deposition (CVD), ..etc. [4].

Experimental:

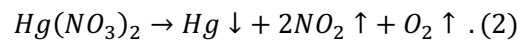
Mercury nitrate (Hg(NO₃)₂) molecular weight (324.60 g/mole) dissolved in ionized water by molarity (0.1 mole) doped ZnO with (3, 6, and 9)% concentrations in zinc nitrate solution by volume doping, deposited on glass substrate at 400 °C, using (CSP)



technique. Pure ZnO can be syntheses from zinc nitrate of the component (Zn (NO₃)₂.6H₂O) according to the chemical following equations [5]:



By heating of substrate, mercury nitrate decomposes according to the equation [6]:



- **Results and Discussions:**
- **Structural Properties:**

Figure (2) shows XRD of ZnO and mercury doped zinc oxide (ZnO:Hg) for doping concentration (3, 6, and 9)%, where the plane of (002) is the extinguished plane which appear from the XRD for the thin films.

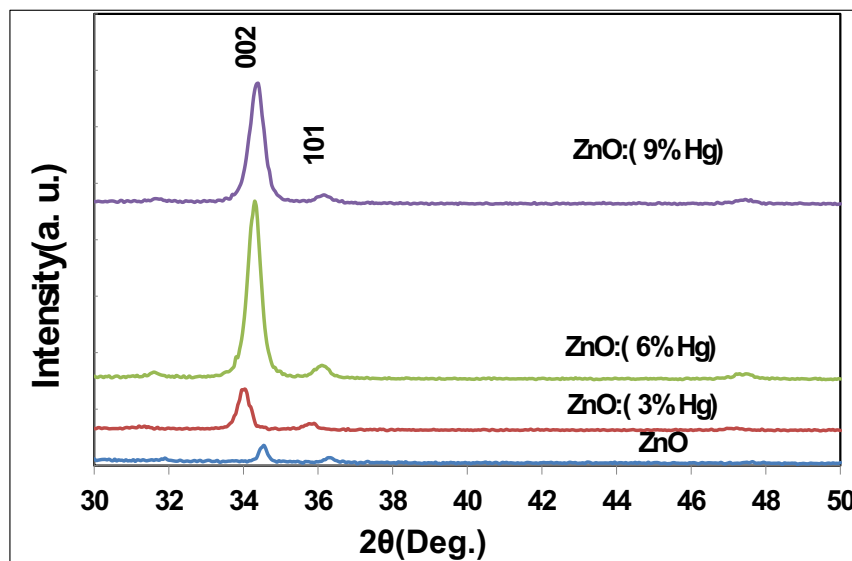


Fig. (1): XRD patterns for thin films of undoped ZnO and ZnO:Hg thin films with different doping concentration (3, 6 and 9)%Wt.

For small ions the interplanar spacing d was decreased [Michael, 2012; Murphy et al., 2004], While for big ions d was increased [7]. The relation between interplanar spacing (d) and Bragg's angle (θ), according to Bragg's equation [8]:

$$n\lambda = 2d \sin\theta \dots (3)$$

Where θ : Bragg's angle, λ : the wavelength of the X-rays, n is an integer and it is the order of reflection, and d is the distance between the lattice planes (interplanar spacing). So that doping of mercury leads to shift to the minus direction in the output peak position of 2θ in x-axis of XRD pattern as shown in table (1), because the ion size of mercury (0.151 nm) is big comparison with the ionic radius of zinc oxide Zn^{2+} (0.074 nm) [7]. The increasing of d causes increasing the constants of lattice (a and c) as demonstrated in the table (1).

Table (1): ZnO and ZnO:Hg thin films Structural parameters and lattice constants.

hkl	Samples	2θ (deg.)	$d(nm)$	$\beta(FWHM)$ (deg.)	$a(nm)$	$c(nm)$	D_{XRD} (nm)	D_{AFM}
	ZnO	34.540	0.26035	0.2427	0.32500	0.52070	35.8	72
002	ZnO:(3% Hg)	34.550	0.26329	0.1231	0.32867	0.52658	39	185
	ZnO:(6% Hg)	34.300	0.26123	0.4166	0.32610	0.52246	20.9	164
	ZnO:(9% Hg)	34.368	0.26072	0.4698	0.32548	0.52145	18.5	153
	ASTM	34.421	0.26033		0.32498	0.52066		

Where: ASTM(the American Society for Testing and Materials)[9], the crystallite size D_{XRD} of the thin films calculated by Sherrer's equation (3) [10], were shown in figure (3).

$$D_{XRD} = \frac{k\lambda}{\beta_D \cos(\theta)} \quad \dots (4)$$

The crystallite size value increases for ZnO:(3% Hg) due to the decreasing of dislocation density which means enhancement and decreasing of defect in the lattice, then the increasing of mercury doping concentration become as a defects in the lattice which leads to increase the dislocation density, so that the crystallite size decreased.

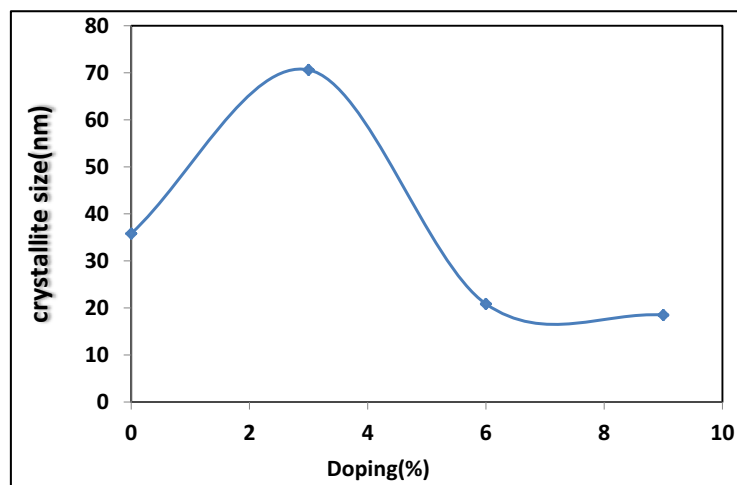


Fig. (2) Average crystallite size for (002) plane of ZnO and ZnO:Hg thin films vs.doping concentration.

(2-D) and granularity distribution of Atomic Force Microscope (AFM) images for ZnO and ZnO:Hg thin films reveals in Figure (4). The surface characteristics are significant features of electronic devices which are used for applications like gas sensors [11, 12].

AFM is used to determine average grain size and roughness average, where the average grain size measured by AFM is shown in table (1), where the maximum value was in ZnO:(3% Hg) as the result of crystallite size which was obtained by XRD, the surface topographic of the thin films as roughness average found increased with the doping increasing of mercury which is found to be around (1.34 to 14.884) nm.

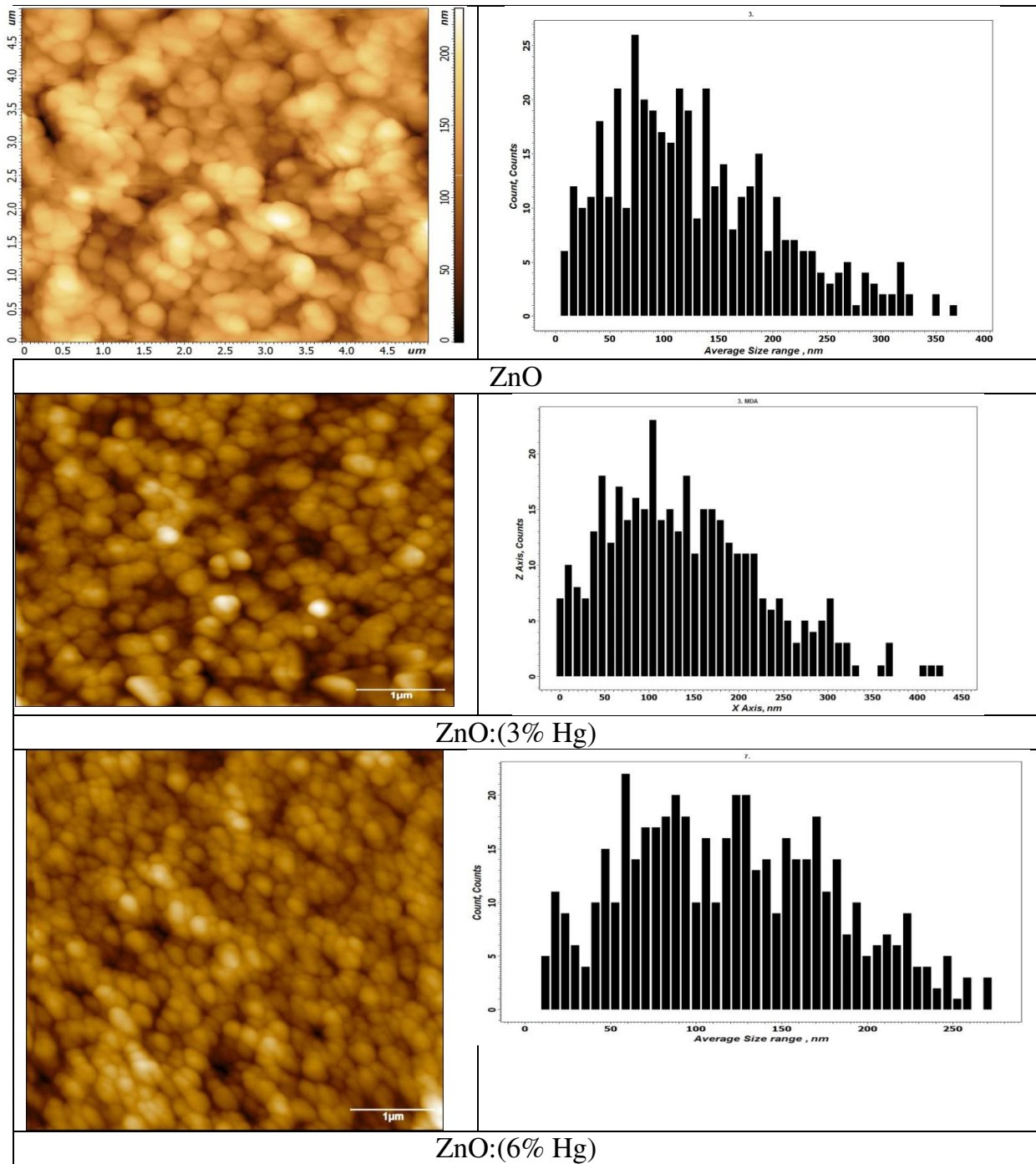


Fig. (3): Granularity distribution and 2-D AFM images of the ZnO and ZnO:Hg thin films with doping concentration (3, and 6)% Wt.

Sensing Properties:

The ZnO pure and ZnO:Hg thin films has been tested as a sensor for CO₂ gas, Figure (5) shows the electrical resistance of the thin films versus operating time at room temperature (RT), The resistance of the thin films is decreased with increasing of doping concentration of mercury in ZnO.

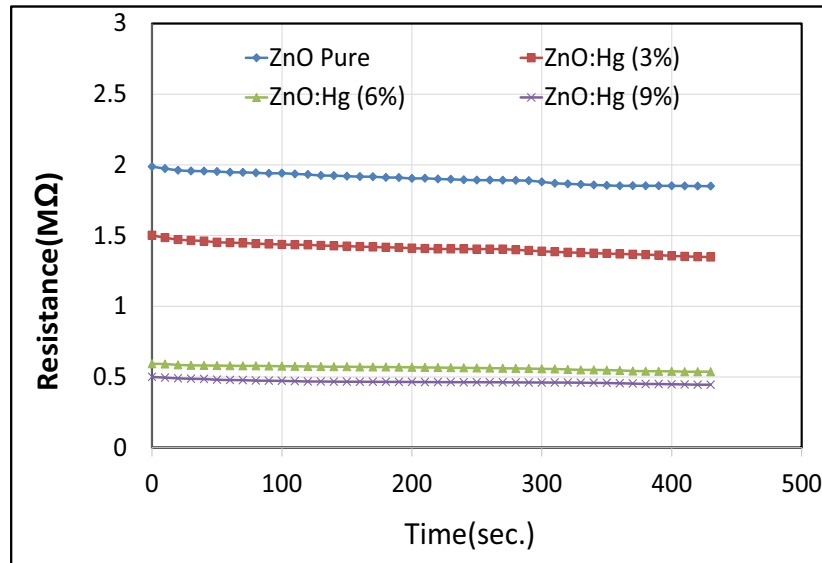


Fig. (4) Resistance of ZnO and ZnO:Hg thin films with doping concentration (3, 6 and 8)%Wt. as a function of operating time .

The sensitivity of sensors can calculate depending on the resistance of the films by using the equation [13, 14]:

$$S = \frac{|R_g - R_a|}{R_a} \times 100 \quad \dots (5)$$

Where: R_a is the thin film electric resistance in the air, and R_g is the electric resistance of the thin film in gas presence.

Figure (6) reveals the sensitivity of ZnO and ZnO:Hg films is increased according to the increasing of mercury doping in the films due to increasing of electrons caused by mercury concentrations.

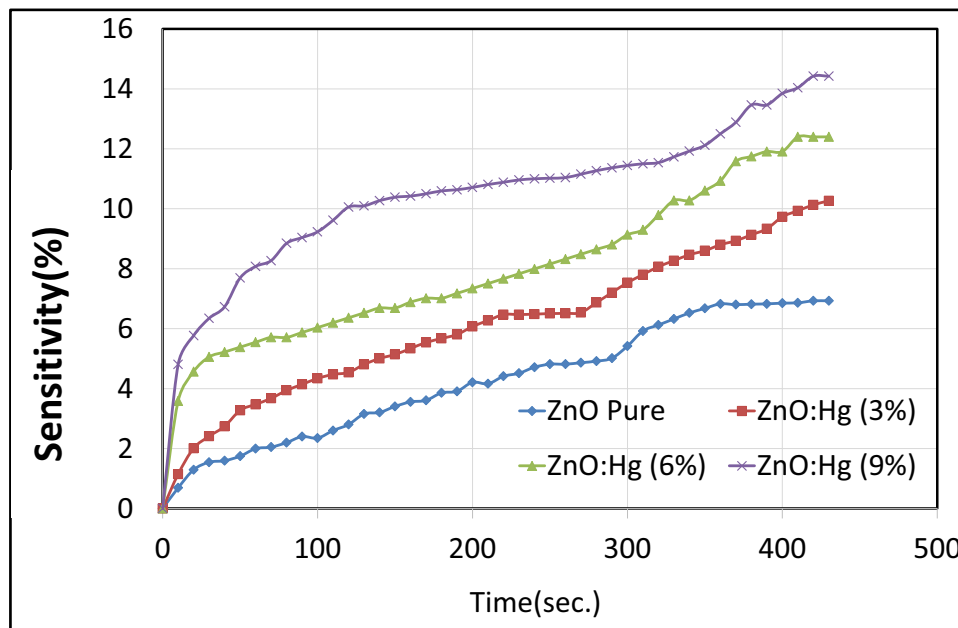


Fig. (5) Sensitivity of ZnO and ZnO:Hg thin films with doping concentration (3, 6 and 8)%Wt. as a function of operating time .

Conclusions:

Doping concentration of mercury added to ZnO leads to shift in peaks of (002) plane of XRD diagrams because of large ionic radius of mercury, crystallite size and grain size increased at ZnO:(3% Hg) the decreases with the increase of mercury doping concentrations. Spray pyrolysis technique is used efficiently grow ZnO and ZnO:Hg thin films. The sensitivity of the films for CO₂ gas increased with the increasing of mercury doping concentration.

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