

Structural and Morphological Studies for ZnO:SnO₂ Composite Thin Films

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Abstract: In the present work, structural properties have been studied for ZnO, SnO₂, ZnO: SnO₂ composite thin film prepared by spray pyrolysis technique deposition at substrate glass with different deposition conditions, volume ratios(50%:50%,70%:30%,90%:10%), Substrate temperature (400 and 450°C), incident angle spray (0 and 45)degree. The X-ray diffraction technique has showed that all prepared films are polycrystalline structure type of hexagonal with preferred orientation of plan (002) direction for all prepared thin films (ZnO, ZnO:SnO₂ composite) except SnO₂ thin films are polycrystalline structure type of tetragonal with preferred orientation of plane (110), the results obtained by X- ray diffragrams show that the thin film structure has an average grain size between (2.4 to 46 nm) and uniform homogeneity by added tin oxide to zinc oxide , the results show high crystalline with deferent conditions deposition. Surface analysis by SEM and AFM has been used to understand the effect of the different conditions deposition on morphology properties of the samples. the SEM micrographs show needle – like, fiber – like, hexagonal nano rods, rich particles (high growth) and homogeneity, uniform distribution, high growth. The results showed an increase of the average grain size with roughness increasing, and this leads to obtain a high surface area.

Keywords: Composite thin films; ZnO: SnO₂ thin films; Structural properties; Morphological studies.

Introduction

Zero and one dimensional nanostructures of binary metal oxides such as SnO₂, ZnO and TiO₂ have attracted great interest owing to their unique properties and potential use in different diverse applications [1]. ZnO and SnO₂ belong to wide direct band gap semiconductors, and their band gaps are 3.4 and 3.6 eV respectively [2, 3]. Zinc and tin oxides have attracted considerable attention and many investigators exploited various synthesis methods to couple and to obtain nano composites of ZnO and SnO₂ [4].

Composite materials are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic within the finished structure composite thin films are a new area of study with many applications, e.g. metal oxide thin films in high density magnetic recording media. Engineering the processing, microstructure and properties of these thin films is of great importance Surface diffusion and self-shadowing effects are found to play an important role in determining various film microstructures under different processing conditions [5].

The conductometric semiconducting metal oxide gas sensors currently constitute one of the most investigated groups of gas sensors. They have attracted much attention in the field of gas sensing under atmospheric conditions due to their low cost and flexibility in production, simplicity of their use and large number of detectable gases possible application fields. In addition to the conductivity change of gas-sensing material, the detection of this reaction can be performed by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy released by the gas/solid interaction [5].

Experimental Work

A. Films Preparation

The ZnO pure, SnO₂ pure and ZnO: SnO₂ composite thin films were deposited by spray pyrolysis technique using homemade equipment as illustrated in the Figure (1) with different parameters show in the table (1).

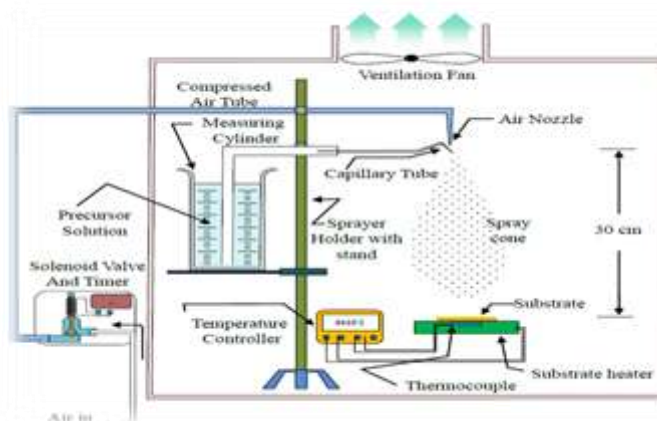


Fig. (1) The diagram of spray pyrolysis equipment.

Table (1) Spray pyrolysis process parameters for the deposition Of ZnO:SnO₂ composite thin films.

| Spray parameters | Optimum value/Item |
|-------------------------------------|--------------------|
| Nozzle diameter | 0.3 mm |
| Nozzle-substrate distance | 32 cm |
| Precursor solution concentration | 0.1M |
| Solvent | Distilled water |
| Solution flow rate | 3 ml/min |
| Carrier gas | Nitrogen |
| Gas pressure | 4 bar |
| Substrate temperature | (400,450)°C |
| Incident spray angle (for nozzle) | (0,45) degree |

ZnO: SnO₂ thin films composite were prepared by using a mixing of an aqueous solution of Zinc Chloride (ZnCl₂.5H₂O) with concentration (0.1) M and Tin Chloride (SnCl₄.2H₂O) with concentration (0.1) according to the different conditions illustrated in the table (2), dissolved in 100 ml of distilled water. The mixture was stirred by (magnetic stirrer) for 30 min.

Table (2) Conditions of deposition ZnO:SnO₂ thin film composite by spray pyrolysis.

| Volume ratio | Incident angle | Substrate temperature |
|-----------------------------------|----------------|-----------------------|
| ZnO(100%), SnO ₂ (0%) | 0° & 45° | 400 & 450 °C |
| ZnO(0%), SnO ₂ (100%) | 0° & 45° | 400 & 450 °C |
| ZnO (50%), SnO ₂ (50%) | 0° & 45° | 400 & 450 °C |
| ZnO(70%), SnO ₂ (30%) | 0° & 45° | 400 & 450 °C |
| ZnO(90%), SnO ₂ (10%) | 0 ° & 45° | 400 & 450 °C |

B. Material Characterizations

X- Ray Diffraction (XRD)

The structure analysis and lattice parameters of films were carried out by analyzing the x-ray diffraction patterns obtained via diffractometer of target Cu K_α, with wavelength of 1.5406 Å and glancing angle (2θ) in the range of 10 to 60 degrees.

Figures (2to5) show the XRD patterns for (ZnO:SnO₂) composite thin films with different deposition conditions (volume ratio, substrate temperature, incident angle for spray pyrolysis), the resultant patterns give an indication about

the structure crystallinity, the films have polycrystalline structure of the hexagonal ZnO standards peaks with preferred orientation at (002) plane for ZnO ratio of (100%, 50%, 70% and 90%) and the tetragonal structure of SnO₂ with preferred orientation at (110) plane, the growth as well as the crystallization of zinc oxide much higher than tin oxide, especially after adding the tin oxide to zinc oxide at different rates. The optimum ratio was (ZnO 90% : SnO₂ 10 %), at the incident angle of sprayer of (45°) degree. Figure (5) shows that this ratio represents the highest average grain size (highest crystallization) in prepared thin film and this confirms that the addition of tin oxide by simple and specific lead to an increase of crystallization, the adding of SnO₂ will affect the crystallization, new peaks will appear by increasing incident angle to 45 degree this led to increase of crystallization and reveal new planes of directions. The preferred orientations data and average grain size for thin films prepared by spray pyrolysis with different conditions tabulated in the tables (3) to (7).

X-ray diffraction could be used to define the preferred orientation, and from the diffractograms one can calculate the average grain size and determine whether the deposited films suffer from stress or not.

The average grain size calculated using Debye-Scherrer formula was nano structure, The single line method is one of the several line profile analysis methods based on a Voigt function to determine the size-strain parameters (microstrains and crystallite sizes), The average grain size (g), which can be estimated using the Scherrer's formula [6] :

$$g = (0.94 \lambda) / [\Delta (2 \theta) \cos \theta] \dots\dots\dots(1)$$

where:

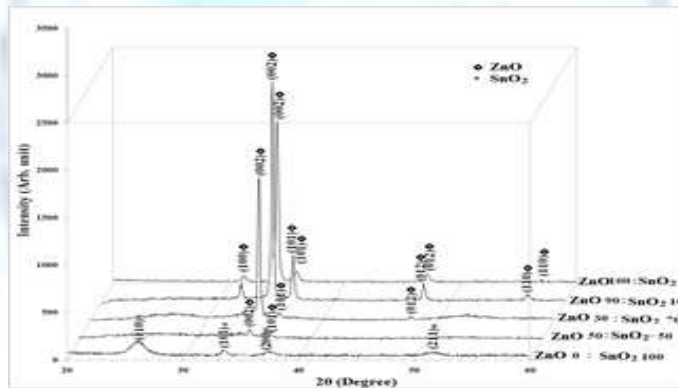
λ : is the x-ray wavelength (Å) .

$\Delta (2 \theta)$: FWHM (radian) .

θ : Bragg diffraction angle of the XRD peak (degree) .

The micro strains are caused during the growth of thin films , and will be raised from stretching or compression in the lattice to make a deviation in the c-lattice constant of the hexagonal structure from the ASTM value. So the strain broadening is caused by varying displacements of the atoms with respect to their reference lattice position [6]. This strain can be calculated from the formula:

$$\delta = [| C_{ASTM} - C_{XRD} | / C_{ASTM}] * 100\% \dots\dots\dots(2)$$



Fig(2). XRD pattern for ZnO:SnO₂ films with different ratio at T=400°C and $\alpha=0$.

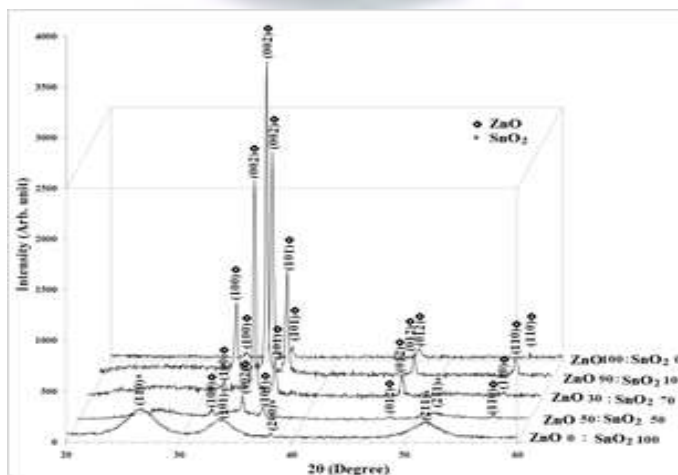


Fig.(3). XRD pattern for ZnO:SnO₂ films with different ratio at Ts=400°C and $\alpha=45^\circ$.

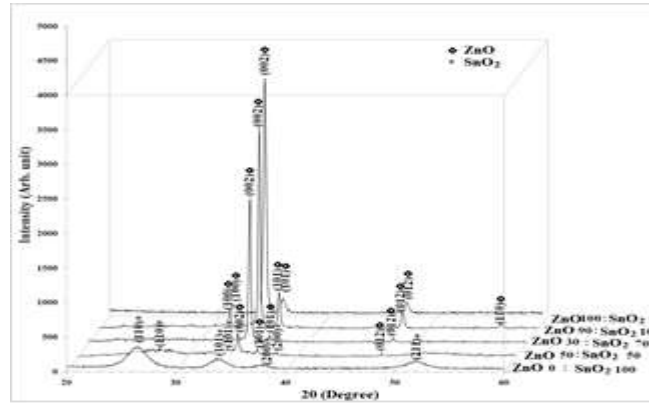


Fig (4). XRD pattern for SnO₂: ZnO films with different ratio at Ts=450°C and α=0.

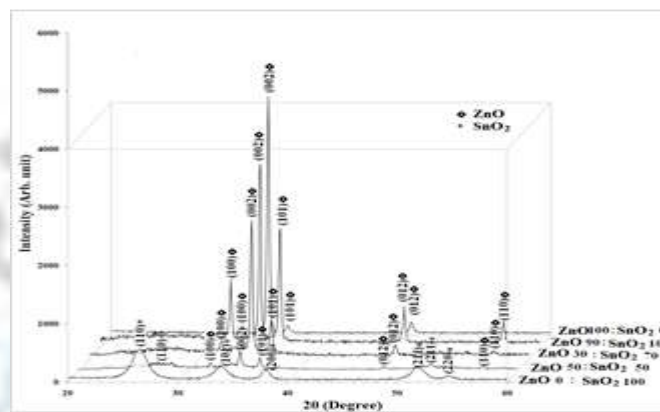


Fig.(5). XRD pattern for ZnO: SnO₂ films with different ratio at Ts=450°C and α=45°.

Table (3) XRD data for 100% ZnO at T = 400 and 450°C and α = 0 & 45°

| Ts (C°) | α (Deg) | 2θ _{exp.} (Deg.) | β (Deg.) | Int. (Arb.U.) | (hkl) | d _{Exp.} (Å°) | d _{Std.} (Å°) | G.S (nm) | Strain *10 ⁻³ |
|---------|---------|---------------------------|----------|---------------|-------|------------------------|------------------------|----------|--------------------------|
| 400 | 0 | 31.247 | 0.419 | 56 | (100) | 2.8602 | 2.8009 | 18.5 | 21.17 |
| | | 34.087 | 0.293 | 1750 | (002) | 2.6281 | 2.5886 | 26.7 | 15.26 |
| | | 35.761 | 0.546 | 90 | (101) | 2.5089 | 2.4635 | 14.4 | 18.43 |
| | | 47.073 | 0.420 | 72 | (012) | 1.9290 | 1.9010 | 19.4 | 14.73 |
| | 45 | 31.381 | 0.356 | 35 | (100) | 2.8481 | 2.8009 | 21.8 | 16.85 |
| | | 34.221 | 0.251 | 2088 | (002) | 2.6182 | 2.5886 | 31.1 | 11.43 |
| | | 35.977 | 0.334 | 70 | (101) | 2.4941 | 2.4635 | 23.4 | 12.42 |
| | | 47.263 | 0.418 | 88 | (012) | 1.9222 | 1.9010 | 19.5 | 11.15 |
| 450 | 0 | 31.298 | 0.399 | 113 | (100) | 2.8557 | 2.8009 | 19.4 | 19.57 |
| | | 34.138 | 0.279 | 3406 | (002) | 2.6243 | 2.5886 | 28.0 | 13.79 |
| | | 35.812 | 0.520 | 182 | (101) | 2.5054 | 2.4635 | 15.1 | 17.01 |
| | | 47.124 | 0.400 | 144 | (012) | 1.9270 | 1.9010 | 20.4 | 13.68 |
| | 45 | 31.432 | 0.339 | 74 | (100) | 2.8438 | 2.8009 | 22.9 | 15.32 |
| | | 34.272 | 0.239 | 4077 | (002) | 2.6143 | 2.5886 | 32.7 | 9.93 |
| | | 36.028 | 0.318 | 144 | (101) | 2.4909 | 2.4635 | 24.7 | 11.12 |
| | | 47.314 | 0.398 | 178 | (012) | 1.9197 | 1.9010 | 20.5 | 9.84 |

Table (4) XRD data for 100% SnO₂ at T=400 and 450°C and α = 0 & 45°

| Ts (C°) | α (Deg) | 2θ _{exp.} (Deg.) | β (Deg.) | Int. (Arb.U.) | (hkl) | d _{Exp.} (Å°) | d _{Std.} (Å°) | G.S (nm) | Strain *10 ⁻³ |
|---------|---------|---------------------------|----------|---------------|--------|------------------------|------------------------|----------|--------------------------|
| 400 | 0 | 26.114 | 1.438 | 177 | (110) | 3.4096 | 3.3487 | 5.3 | 18.2 |
| | | 33.586 | 0.520 | 54 | (101) | 2.6662 | 2.6442 | 15.0 | 8.3 |
| | | 37.502 | 0.919 | 40 | (200) | 2.3963 | 2.3679 | 8.6 | 12.0 |
| | | 51.608 | 1.398 | 31 | (211) | 1.7696 | 1.7640 | 5.9 | 3.2 |
| | 45 | 26.480 | 2.120 | 325 | (110) | 3.3633 | 3.3487 | 3.6 | 4.4 |
| | | 33.880 | 1.640 | 132 | (101) | 2.6437 | 2.6442 | 4.8 | 0.2 |
| 37.880 | | 1.440 | 45 | (200) | 2.3732 | 2.3679 | 5.5 | 2.2 | |
| 51.920 | | 2.000 | 101 | (211) | 1.7597 | 1.7640 | 4.2 | 2.4 | |
| 450 | 0 | 26.635 | 3.199 | 264 | (110) | 3.3441 | 3.3487 | 2.4 | 1.4 |
| | | 33.705 | 2.479 | 166 | (101) | 2.6570 | 2.6442 | 3.2 | 4.8 |
| | | 38.169 | 1.020 | 31 | (200) | 2.3560 | 2.3679 | 24.7 | 5.0 |
| | | 51.860 | 2.840 | 144 | (211) | 1.7616 | 1.7640 | 2.9 | 1.4 |
| | 45 | 26.584 | 1.621 | 511 | (110) | 3.3504 | 3.3487 | 4.7 | 0.5 |
| | | 33.971 | 1.459 | 220 | (101) | 2.6368 | 2.6442 | 5.4 | 2.8 |
| | | 38.067 | 0.771 | 173 | (200) | 2.3620 | 2.3679 | 10.3 | 2.5 |
| | | 51.926 | 1.337 | 211 | (211) | 1.7595 | 1.7640 | 6.2 | 2.6 |
| | | 54.727 | 0.891 | 58 | (220) | 1.6759 | 1.6743 | 9.5 | 1.0 |

Table (5) XRD data for ZnO 90% and SnO₂ 10% ZnO at Ts=400 and 450°C and α=0 and 45°

| Ts (C°) | α (Deg) | 2θ _{exp.} (Deg.) | β (Deg.) | Int. (A.U.) | (hkl) | Phase | d _{Exp.} (Å°) | d _{Std.} (Å°) | G.S (nm) | Strain *10 ⁻³ |
|---------|---------|---------------------------|----------|-------------|-------|-------|------------------------|------------------------|----------|--------------------------|
| 400 | 0 | 32.090 | 0.321 | 197 | (100) | ZnO | 2.7870 | 2.8009 | 24.3 | 4.96 |
| | | 34.750 | 0.224 | 2400 | (002) | ZnO | 2.5795 | 2.5886 | 35.0 | 3.52 |
| | | 36.420 | 0.267 | 488 | (101) | ZnO | 2.4650 | 2.4635 | 29.5 | 0.61 |
| | | 47.820 | 0.324 | 183 | (012) | ZnO | 1.9006 | 1.9010 | 25.3 | 0.21 |
| | | 56.750 | 0.375 | 72 | (110) | ZnO | 1.6209 | 1.6171 | 22.7 | 2.35 |
| | 45 | 31.860 | 0.221 | 588 | (100) | ZnO | 2.8066 | 2.8009 | 35.2 | 2.04 |
| | | 34.550 | 0.189 | 2650 | (002) | ZnO | 2.5940 | 2.5886 | 41.5 | 2.09 |
| | | 36.360 | 0.189 | 851 | (101) | ZnO | 2.4689 | 2.4635 | 41.7 | 2.19 |
| | | 47.640 | 0.253 | 202 | (012) | ZnO | 1.9073 | 1.9010 | 32.3 | 3.31 |
| | | 56.700 | 0.323 | 142 | (110) | ZnO | 1.6222 | 1.6171 | 26.3 | 3.15 |
| 450 | 0 | 31.950 | 0.311 | 198 | (100) | ZnO | 2.7989 | 2.8009 | 25.0 | 0.71 |
| | | 34.640 | 0.215 | 2500 | (002) | ZnO | 2.5874 | 2.5886 | 36.5 | 0.46 |
| | | 36.440 | 0.236 | 432 | (101) | ZnO | 2.4636 | 2.4635 | 33.4 | 0.04 |
| | | 47.750 | 0.315 | 208 | (012) | ZnO | 1.9032 | 1.9010 | 26.0 | 1.16 |
| | | 56.740 | 0.356 | 45 | (110) | ZnO | 1.6211 | 1.6171 | 23.9 | 2.47 |
| | 45 | 32.100 | 0.192 | 983 | (100) | ZnO | 2.7861 | 2.8009 | 40.6 | 5.28 |
| | | 34.800 | 0.177 | 2850 | (002) | ZnO | 2.5759 | 2.5886 | 44.3 | 4.91 |
| | | 36.590 | 0.181 | 1841 | (101) | ZnO | 2.4539 | 2.4635 | 43.5 | 3.90 |
| | | 47.870 | 0.224 | 559 | (012) | ZnO | 1.8987 | 1.9010 | 36.6 | 1.21 |
| | | 56.810 | 0.296 | 338 | (110) | ZnO | 1.6193 | 1.6171 | 28.7 | 1.36 |

Table (6) XRD data for ZnO 70% and SnO₂ at Ts = 400 and 450°C and α = 0 and 45°

| Ts (C°) | α (Deg) | 2θ _{exp.} (Deg.) | β (Deg.) | Int. (A.U.) | (hkl) | Phase | d _{Exp.} (Å°) | d _{Std.} (Å°) | G.S (nm) | Strain *10 ⁻³ |
|---------|---------|---------------------------|----------|-------------|-------|-------|------------------------|------------------------|----------|--------------------------|
| 400 | 0 | 34.600 | 0.299 | 1500 | (002) | ZnO | 2.5903 | 2.5886 | 26.2 | 0.66 |
| | | 36.360 | 0.394 | 68 | (101) | ZnO | 2.4689 | 2.4635 | 20.0 | 2.19 |
| | | 47.750 | 0.419 | 34 | (012) | ZnO | 1.9032 | 1.9010 | 19.5 | 1.16 |
| | 45 | 31.990 | 0.360 | 117 | (100) | ZnO | 2.7955 | 2.8009 | 21.6 | 1.93 |

| | | | | | | | | | | |
|-----|----|--------|-------|------|-------|-----|--------|--------|------|------|
| | | 34.700 | 0.250 | 2200 | (002) | ZnO | 2.5831 | 2.5886 | 31.4 | 2.12 |
| | | 36.540 | 0.360 | 368 | (101) | ZnO | 2.4571 | 2.4635 | 21.9 | 2.60 |
| | | 47.760 | 0.400 | 205 | (012) | ZnO | 1.9028 | 1.9010 | 20.5 | 0.95 |
| 450 | 0 | 34.780 | 0.271 | 2100 | (002) | ZnO | 2.5773 | 2.5886 | 28.9 | 4.37 |
| | | 36.550 | 0.322 | 96 | (101) | ZnO | 2.4565 | 2.4635 | 24.5 | 2.84 |
| | | 47.900 | 0.311 | 65 | (012) | ZnO | 1.8976 | 1.9010 | 26.3 | 1.79 |
| | 45 | 32.040 | 0.283 | 227 | (100) | ZnO | 2.7912 | 2.8009 | 27.5 | 3.46 |
| | | 34.760 | 0.234 | 2400 | (002) | ZnO | 2.5788 | 2.5886 | 33.5 | 3.79 |
| | | 36.550 | 0.281 | 602 | (101) | ZnO | 2.4565 | 2.4635 | 28.0 | 2.84 |
| | | 47.820 | 0.283 | 62 | (012) | ZnO | 1.9006 | 1.9010 | 28.9 | 0.21 |

Table (7) XRD data for ZnO 50% SnO₂50% Ts=400 and 450°C and α=0 and 45°.

| Ts (C°) | α (Deg) | 2θ _{exp.} (Deg.) | β (Deg.) | Int. (A.U.) | (hkl) | Phase | d _{Exp.} (Å°) | d _{Std.} (Å°) | G.S (nm) | Strain *10 ⁻³ |
|---------|---------|---------------------------|----------|-------------|------------------|------------------|------------------------|------------------------|----------|--------------------------|
| 400 | 0 | 26.720 | 3.144 | 51 | (110) | SnO ₂ | 3.3336 | 3.3487 | 2.4 | 4.51 |
| | | 32.120 | 0.357 | 49 | (100) | ZnO | 2.7869 | 2.8009 | 21.8 | 5.00 |
| | | 33.920 | 0.832 | 72 | (101) | SnO ₂ | 2.6431 | 2.6442 | 9.4 | 0.42 |
| | | 34.800 | 0.297 | 120 | (002) | ZnO | 2.5777 | 2.5886 | 26.4 | 4.21 |
| | | 36.620 | 0.297 | 69 | (101) | ZnO | 2.4539 | 2.4635 | 26.5 | 3.90 |
| | | 52.100 | 1.664 | 11 | (211) | SnO ₂ | 1.7540 | 1.7640 | 5.0 | 5.67 |
| | | 56.970 | 0.357 | 14 | (110) | ZnO | 1.6165 | 1.6171 | 23.8 | 0.37 |
| | 45 | 26.760 | 3.126 | 76 | (110) | SnO ₂ | 3.3313 | 3.3487 | 2.5 | 5.20 |
| | | 31.940 | 0.416 | 75 | (100) | ZnO | 2.8018 | 2.8009 | 18.7 | 0.32 |
| | | 34.010 | 0.357 | 81 | (101) | SnO ₂ | 2.6360 | 2.6442 | 21.9 | 3.10 |
| | | 34.660 | 0.254 | 250 | (002) | ZnO | 2.5885 | 2.5886 | 30.9 | 0.04 |
| | | 36.460 | 0.297 | 128 | (101) | ZnO | 2.4644 | 2.4635 | 26.5 | 0.37 |
| | | 47.790 | 0.535 | 42 | (012) | ZnO | 1.9031 | 1.9010 | 15.3 | 1.10 |
| | | 52.180 | 2.556 | 41 | (211) | SnO ₂ | 1.7529 | 1.7640 | 3.3 | 6.29 |
| 56.880 | 0.357 | 22 | (110) | ZnO | 1.6187 | 1.6171 | 23.8 | 0.99 | | |
| 450 | 0 | 26.760 | 3.126 | 76 | (110) | SnO ₂ | 3.3313 | 3.3487 | 2.5 | 5.20 |
| | | 26.890 | 2.685 | 65 | (110) | SnO ₂ | 3.3153 | 3.3487 | 2.9 | 9.97 |
| | | 31.990 | 0.335 | 63 | (100) | ZnO | 2.7980 | 2.8009 | 23.2 | 1.04 |
| | | 33.870 | 0.297 | 89 | (101) | SnO ₂ | 2.6463 | 2.6442 | 26.3 | 0.79 |
| | | 34.690 | 0.297 | 300 | (002) | ZnO | 2.5862 | 2.5886 | 26.4 | 0.93 |
| | | 36.460 | 0.238 | 102 | (101) | ZnO | 2.4644 | 2.4635 | 33.1 | 0.37 |
| | | 38.100 | 0.178 | 44 | (200) | SnO ₂ | 2.3623 | 2.3679 | 44.5 | 2.36 |
| | | 47.790 | 0.178 | 29 | (012) | ZnO | 1.9031 | 1.9010 | 46.0 | 1.10 |
| | 45 | 51.750 | 2.556 | 31 | (211) | SnO ₂ | 1.7667 | 1.7640 | 3.3 | 1.53 |
| | | 56.965 | 0.238 | 25 | (110) | ZnO | 1.6153 | 1.6171 | 35.8 | 1.11 |
| | | 26.840 | 2.912 | 66 | (110) | SnO ₂ | 3.3190 | 3.3487 | 2.6 | 8.87 |
| | | 32.020 | 0.357 | 91 | (100) | ZnO | 2.7956 | 2.8009 | 21.8 | 1.89 |
| | | 33.920 | 0.357 | 100 | (101) | SnO ₂ | 2.6426 | 2.6442 | 21.9 | 0.61 |
| | | 34.720 | 0.237 | 400 | (002) | ZnO | 2.5839 | 2.5886 | 33.1 | 1.82 |
| 45 | 36.520 | 0.297 | 177 | (101) | ZnO | 2.4603 | 2.4635 | 26.5 | 1.30 | |
| | 38.180 | 0.357 | 35 | (200) | SnO ₂ | 2.3574 | 2.3679 | 22.2 | 4.43 | |
| | 47.880 | 0.475 | 39 | (012) | ZnO | 1.8998 | 1.9010 | 17.2 | 0.63 | |
| | 52.100 | 2.080 | 38 | (211) | SnO ₂ | 1.7556 | 1.7640 | 4.0 | 4.76 | |
| | 56.840 | 0.524 | 29 | (110) | ZnO | 1.6199 | 1.6171 | 16.2 | 1.73 | |

Figure (6) show comparing between the volume ratio and average grain size for all preferred orientation with temperature substrate (T) and incident angle (α), as it's can be seen the increasing in the volume ratio with the average grain size.

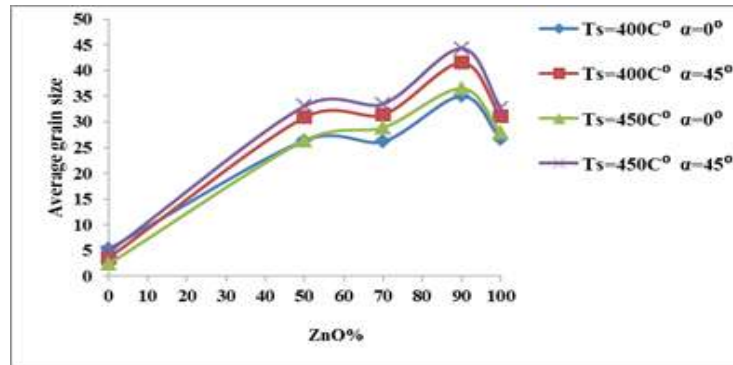


Fig. (6). Effect of ZnO wt.% on the average grain size.

C. Surface Morphology

Atomic Force Microscopy (AFM)

The surface morphology of ZnO, SnO₂ and ZnO:SnO₂ composite thin films were analyzed using an atomic force microscopy (AA-3000). It is known that the surface morphology of the films influences their properties as an important factors for applications like gas sensing, the increasing in surface roughness of the films leads to increase in sensing properties, therefore it is very important to investigate the surface morphology of the films, the surface morphology of the ZnO:SnO₂ composite thin films with different deposition condition at specific substrate temperature measured by AFM are illustrated in the figures (7 to 11). The analysis of the results can give an excellent value for average grain size and the surface roughness, these results are tabulated in the table (8). Surface roughness of the samples shows score of heights and bottoms (brightness and darkness color) as shown in the images, the increase of the number of dips and rises within the space give rise of roughness and it can be noticed through the sample image as well as the homogeneity of the thin film surface.

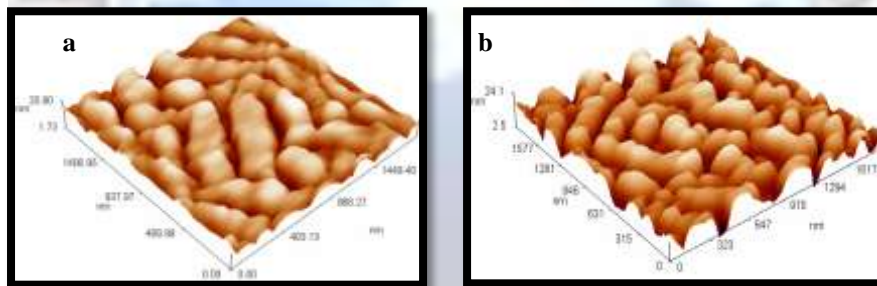


Fig. (7). AFM images for ZnO100%: (a) incident angle (0), substrate temperature (450°C), (b) incident angle (45°), substrate temperature 450°C.

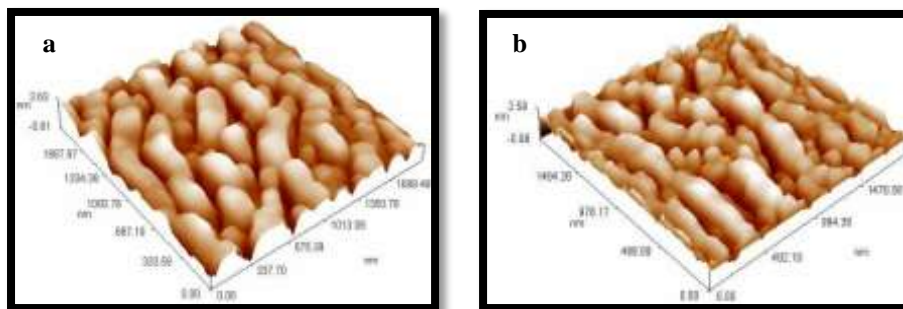


Fig. (8). AFM images for SnO2 100%: (a) incident angle (0), substrate temperature (450°C), (b) incident angle (45°), substrate temperature 450°C.

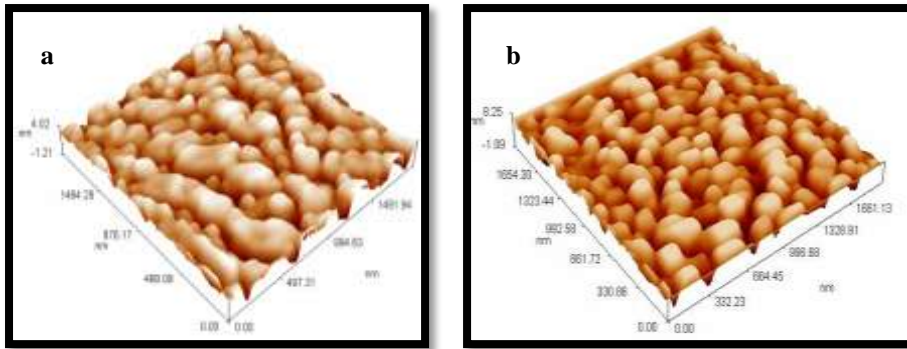


Fig. (9).AFM images for ZnO 50%,SnO₂50%: (a) incident angle (0),substrate temperature (450°C), (b) incident angle (45°),substrate temperature 450°C.

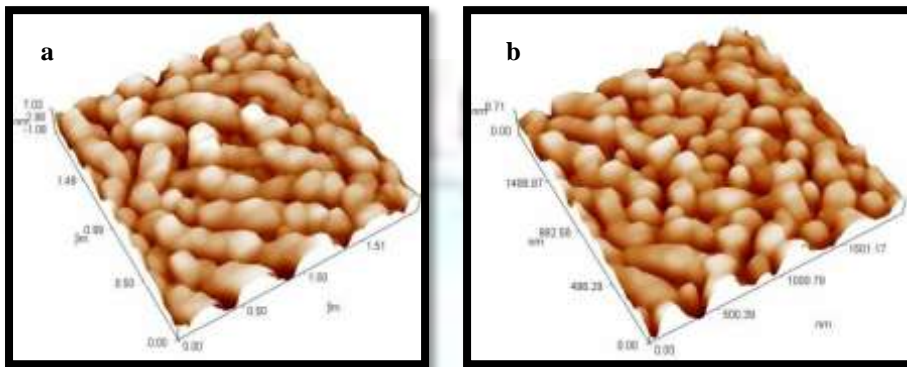


Fig.(10).AFM images for ZnO70%,SnO₂30%: (a)incident angle (0),substrate temperature (450°C), (b)incident angle (45°), substrate temperature 450°C.

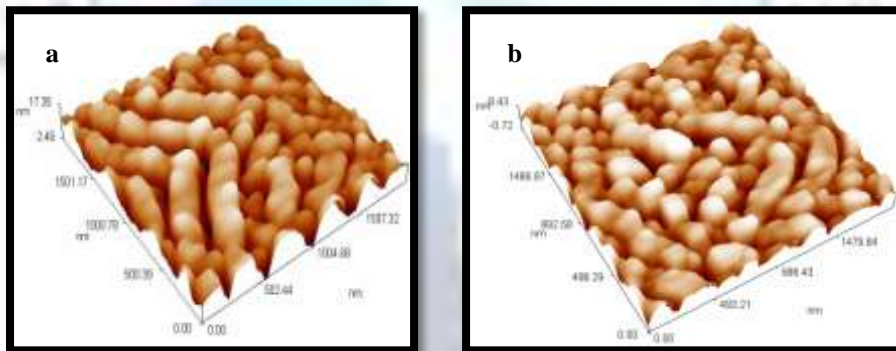


Fig.(11).AFM images for ZnO90%,SnO₂ 10%: (a) incident angle (0), substrate temperature (450°C), (b) incident angle (45°), substrate temperature 450°C.

Table (8) Roughness and grain size at incident angle (0,45) for all prepared samples

| Volume ratio | Incident angle | RMS Roughness | average Grain Size(nm) |
|-----------------------------------|----------------|---------------|------------------------|
| ZnO(100%),SnO ₂ (0%) | 0 | 2.39 | 90.2 |
| ZnO(100%),SnO ₂ (0%) | 45 | 3.9 | 107.69 |
| ZnO (0%), SnO ₂ (100%) | 0 | 0.532 | 80.86 |
| ZnO (0%), SnO ₂ (100%) | 45 | 0.619 | 120.64 |
| ZnO(50%), SnO ₂ (50%) | 0 | 0.726 | 82.29 |
| ZnO(50%), SnO ₂ (50%) | 45 | 1.13 | 100.11 |
| ZnO(70%), SnO ₂ (30%) | 0 | 1.13 | 96.46 |
| ZnO(70%), SnO ₂ (30%) | 45 | 1.22 | 102.93 |
| ZnO(90%), SnO ₂ (10%) | 0 | 1.4 | 91.62 |
| ZnO(90%), SnO ₂ (10%) | 45 | 2.1 | 106.63 |

Increase of the incident angle of the spray to (45) degree for different ratios causes the increase in the average grain size, which in turn leads to increased roughness, as shown the Figure (12).

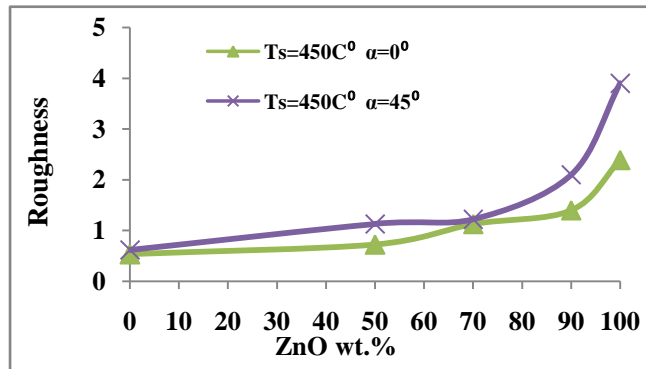


Fig. (12) The effect of ZnO wt.% ratio on the grain size measured by the AFM.

The effect of ZnO wt. %n ratio on the surface roughness of the films shown in the Figure (13).

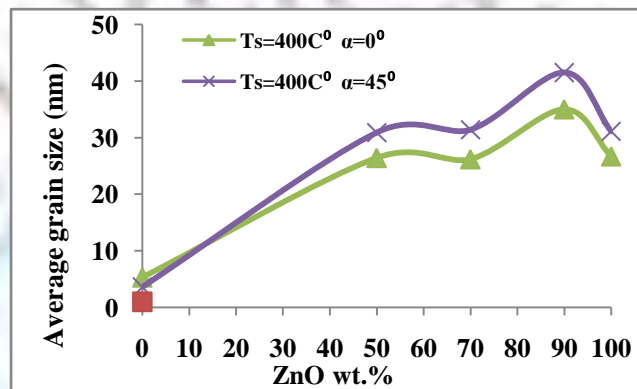


Fig. (13) The effect ZnO wt.% ratio on the roughness measured by the AFM.

D. Scanning Electron Microscopy (SEM)

The morphological properties of all films were investigated using (kyky em3200 model, made in china) scanning electron microscope (SEM, at operating voltage is 20.00 kV). Figures (14 to 18) show the SEM micrographs surface and cross-section for the thin film composite at substrate temperature (450 OC) with incident angle spray (0 & 45) degree, all the micrographs for surface and the cross-section show the homogenous, uniform distribution, high growth. Figure (16 -1) show the needle like. Figure (16-2) show that the fiber like. Figure (17) show the hexagonal nano rods. Figure (18-2) show the rich particles (high growth). In the state of incident angle spray pyrolysis deposited thin films, it is noticed forms like high density rod or needles [7, 8].

It is postulated that in the initial stages of film formation a random distribution of small crystallites is created on the substrate and each crystallite acts as a nucleus for further growth, thus the region behind the crystallite is prevented from receiving metal spray because this region is in the shadow of crystallite. Therefore, as the crystallite grows into a rod, the area behind it is left vacant as far as its shadow extends [9].

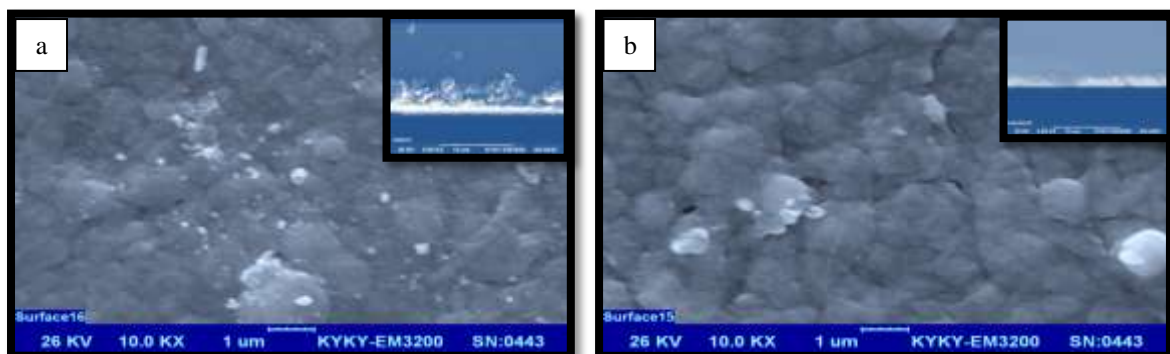


Figure (14).The micrograph SEM surface and the inset image shows the cross section SEM for ZnO 100%: (a) with temperature deposition (450°C) and incident angle (0) degree, (b) with temperature deposition (450°C) and incident angle (45) degree.

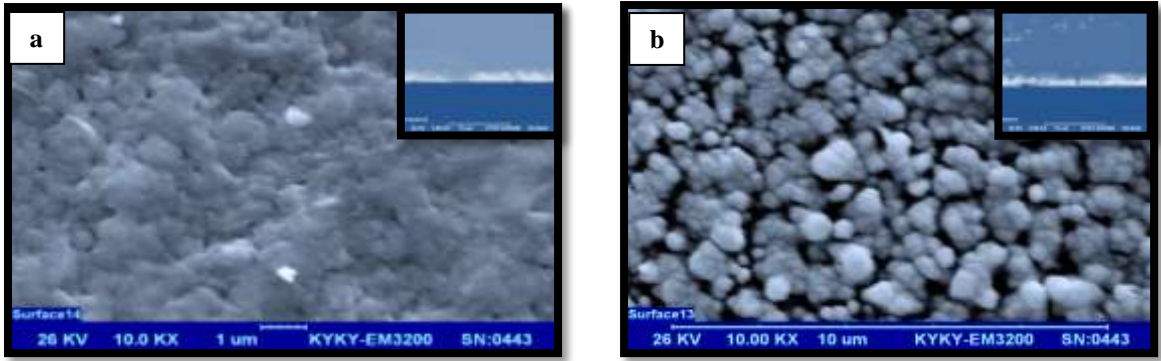


Fig. (15) The micrograph SEM surface and the inset image shows the cross section for SnO₂ 100%: (a) with temperature deposition (450°C) and incident angle (0) degree, (b) with temperature deposition (450°C) and incident angle (45) degree.

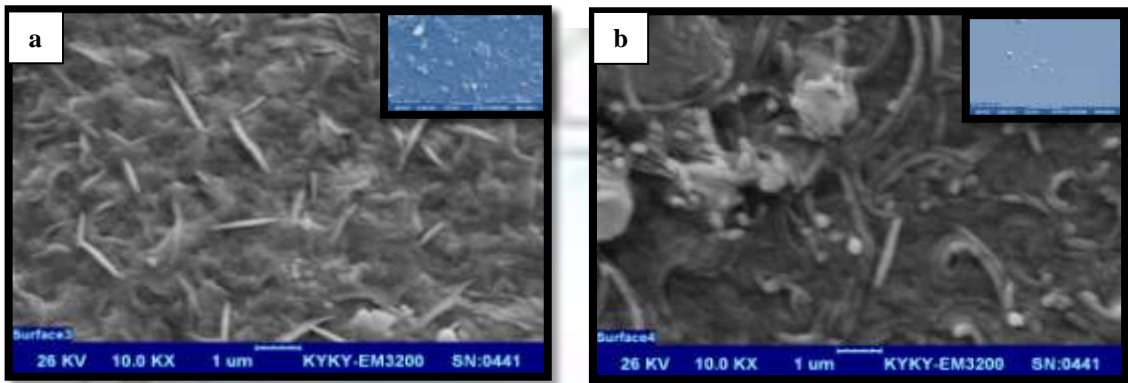


Fig.(16) The micrograph SEM surface and the inset image shows the cross section for ZnO 50% :SnO₂ 50%: (a) with temperature deposition (450°C) and incident angle (0) degree, (b) with temperature deposition (450°C) and incident angle (45) degree.

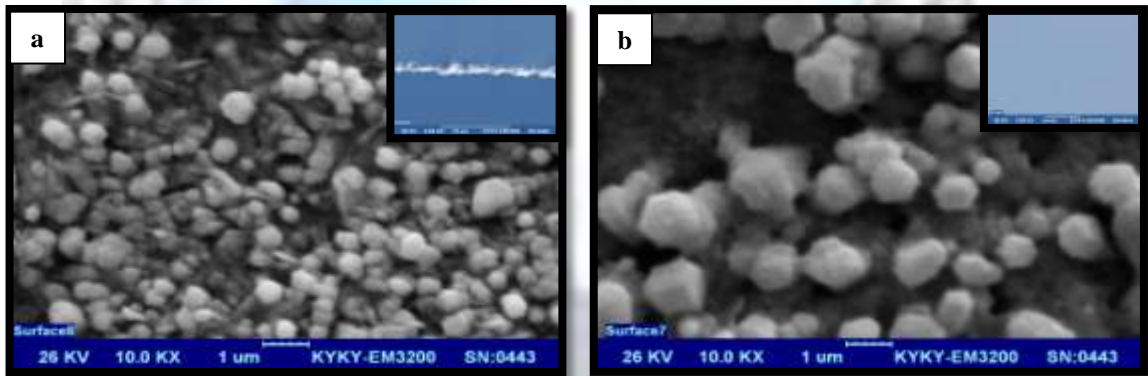


Fig.(17) The micrograph SEM surface and the inset image shows the cross section for ZnO 70% :SnO₂ 30%: (a) with temperature deposition (450°C) and incident angle (0) degree, (b) with temperature deposition (450°C) and incident angle (45) degree.

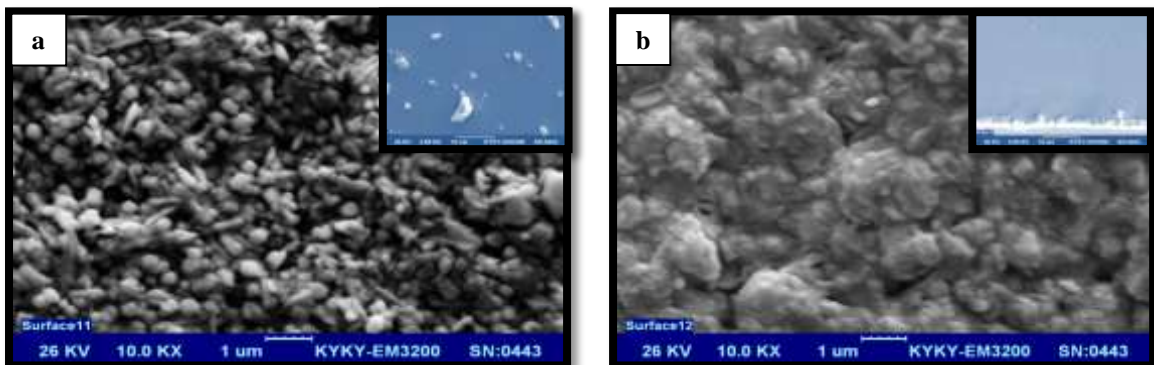


Fig.(18).The micrograph SEM surface and the inset image shows the cross section for ZnO 70% : SnO₂ 30%: (a) with temperature deposition (450°C) and incident angle (0) degree, (b) with temperature deposition (450°C) and incident angle (45) degree.

Conclusion

From the obtained results of the present work we can conclude that:

1. The structure of all thin films was (nanostructure) at optimum condition by chemical spray pyrolysis.
2. From the X-ray diffraction investigation, the crystalline structure of ZnO thin films was a polycrystalline with a hexagonal wurzite structure, the crystalline structure of SnO₂ thin films was a polycrystalline with a tetragonal structure the increasing of volume ratio, incident angle of the spray, increased the substrate temperature caused to increase the average grain size.
3. The surface morphology of the thin films deposited at different condition (volume ratio, substrate temperature, incident angle spray) on glass was high surface roughness and uniform growth.
4. All the thin films prepared show high growth (crystallization) at different conditions especial (ZnO90%:SnO₂ 10%), substrate temperature (450 °C), incident angle (45) degree.

References

- [1] T. Bora, H.H. Kyaw, M. Poyai, J. Dutta, "The 3rd Thailand Nanotechnology Conf. Asian Institute of Technology, 2009.
- [2] Alkaya, R., Kaplan, H., Canbolat, S.S., Hegedus, A, "Comparison of fill factor and recombination losses in amorphous silicon solar cells on ZnO and SnO₂", *Renew. Energ.*, 34, 1595-1599, 2009.
- [3] X. Song, Z. Wang, Y. Liu, C. Wang and L. Li, "A high sensitive gas sensor for ethanol based on Mesoporous ZnO-SnO₂ nanofibres", *Nanotechnology*, 2009.
- [4] C. Liangyuan, B. Shouli, Z. Guojun, L. Dianqing, C. Aifan, C.C. Liu, "Synthesis of ZnO-SnO₂ nano-composites by micro-emulsion and sensing properties for NO₂", *Sens. Actuators, B* 134, 360-366, 2008.
- [5] Korotcenkov, G., "Metal Oxides for Solid-State Gas Sensors: What Determines Our Choice", *Mater. Sci. Eng. B* 7, 139, 1-23, 2007.
- [6] D. A. Neaman, "Semiconductor physics and devices, basic principles", 3d Ed, Mc Grow Hill, New York, 2003.
- [7] J. K. Cho, T. Yamazaki, E. Kita and A. Tasaki, "Magnetic Anisotropy of Co Thin Films Prepared by Oblique Incidence II – Effect of Oxidation–", *Japanese Journal of Applied Physics*, 27, 2, 420, 1988.
- [8] W. E. Weston, T.C. Baker, C. J. Smith, A.L. Chavez, V. K. Grotzky and J. F. Capes, "Physical vapor deposition of chromium and iron", *Journal of Vacuum Science and Technology*, 15, 1, 54, 1978.
- [9] R. T. Kivaisi, "Optical properties of obliquely evaporated aluminium films", *Thin Solid Films*, 97, 153, 1982.