Hydrothermal growth of nanostructured Zinc oxide

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Abstract— *Hydrothermal method was used to prepare ZnO nanostructure .This study haven't used any catalyst or buffer layer before the reaction. The process has taken place inside Teflon lined stainless steel autoclave with volume 100 ml (homemade). ZnO nanotubes, lettuce leaf nanostructure, and nanosticks were successfully synthesized using ZnO nanoparticles (20-30 nanometers) and NaOH (concentrations 6M) which was the starting materials for the chemical reaction under stirring. The suspension was transferred into a Teflon lined sealed stainless steel autoclave and kept at 70 0C for 24, 48, and 72 hour. The influence of the time reaction of synthesis process on the morphology, the crystallinity and structural properties are studied by X-ray diffraction and field emission scanning electron microscope (FE-SEM), the experimental pattern of the films show that diffraction peaks can be assigned to the Wurtzite hexagonal-shaped ZnO as shown in the FE-SEM pictures, also the morphology of the films studied by atomic force microscope (AFM) shows that the prepared thick films have high roughness specially for the powder prepared 48 h .*

Keywords— ZnO, nanotubes, lettuce leaf structure, nanosticks, dislocation density.

I. INTRODUCTION

Zinc oxide(ZnO) has extensive commercial use during the past 100 years .The low size (Nano, micro)materials have interesting attention due to their size dependent properties and wide range of applications in different fields such as industry, health and environment[1-5] with special important applications in optoelectronics, nano/microelectronics, sensors, transducers, and biomedicine . In the group of II-VI compound semiconductors, ZnO has received great attention due to its remarkable combination of physical and optical properties. Its wide band gap (3.37 eV) at room temperature, high excitation binding energy (60 meV) [6,7], Nanowires and carbon nanotubes and other nano structures made from different row materials (organic/inorganic).Many preparation methods are now available and give research domain for analyzing and understanding the one-dimensional nanostructures and their future applications[8,9].Extensive efforts are currently devoted to the controlled synthesis and characterization of ZnO nanostructures. Several different methods for the fabrication of ZnO nanostructures (nanorods, nanotubes, nanowire, nanobelts) and arrays have been reported, including hydrothermal synthesis [10-13],Vapour–liquid–solid (VLS), vapour–solid (VS) [14] processes, metal–organic chemical vapor deposition (MOCVD) [15], chemical vapor deposition [16], and solution-liquid-solid growth in organic solvents [17-19].Recently, one-dimensional (1D) zinc oxide materials and differently shaped ZnO nanocrystals have attracted considerable attention due to their unique properties that strongly depend on their size and morphologies and their possible use as building blocks in near-future nanodevices [13]. 2D- and 3D-shaped ZnO nanocrystals will play a significant role as the novel functional units of electronic, electromechanical and optoelectronic devices [20-22], and nanosensors [11, 12 and 23].Novel synthesis routes of ZnO nano rods for solar cells and chemical sensing applications are currently being developed. The latest research efforts are directed towards obtaining alternative, lightweight, flexible nanodevices [15, 24] .the reference[25]was reviewed summarize the condition leading to the growth of different ZnO nanostructures using hydrothermal technique.

II. EXPERIMENTAL

The first step was fabricated the hydrothermal devices (temperature controller, Teflon lined stainless steel autoclave with volume 100 ml (homemade). For synthesis the nanostructure all row materials were analytical grade (>99% shaula Spain).

The Teflon was first cleaned in a diluted HCl (20%) solution for 10 min and then rinsed in de-ionized (DI) water. Subsequently, the substrates were ultrasonically cleaned in an ethanol/acetone (1:1) mixture, then DI water, and dried in air. One gram of ZnO nanoparticles (about 20-30 nm Tecnan Spain) was added to 6 M of NaOH the aqua solution and stirred for twenty minutes, a white suspension appeared, and then the mixture stirred for 1 h without heat then the suspension was transferred into a Teflon lined stainless steel autoclave with a volume of 100 ml, the autoclave was sealed and kept at 70 0C for time reaction 24 h, 48 h and 72 h. After that the autoclave cooled down to room temperature. The obtained powder washed several times in ethanol and distilled water and dried at 80 0C for 30 min then the thick film heated at 500 0C for 1 h to remove residual organic materials. The as-prepared and rapid thermal processed ZnO nanotubes, lettuce leaf structure and nanosticks were characterized by X-ray diffraction (XRD) using a Rigaku (Miniflex II Rigaku, 'D/B max' Japan) X-ray diffractometer equipped with a lettuce leaf structure monochromatized Cu Kα radiation source (λ = 1.5406A°). The operating conditions were 30mA and 40 kV at a scanning rate of 0.02◦/s in the 2θ range from 20◦ to 90◦. Atomic Force Microscope (AFM AA3000) to study the morphology of the film surface and Field Emission Scanning Electron Microscope (FEI-SEM Model Inspect-S50 and Hitachi FE-SEM model s-4160) to study the structural properties of the films.

III. RESULTS AND DISCUSSION

Patterns recorded of XRD in the range of 10–70^{o} with a scanning step of 0.02◦ of ZnO nanostructures prepared from 1g ZnO nanoparticles with 6M NaOH concentration at 70^{o} C for 24 h ,48 h and 72 h are showed in figure 1 .The patterns show the strongest detected (h k l) of major peaks at 2θ values of 31.96◦, 34.61◦,and 36.44◦,are founded corresponding to the lattice planes (1 0 0), (0 0 2),and (1 0 1) respectively for reaction time 24 h and major peaks are at 2θ values of for 48 h ware 32.03◦, 34.730◦, and 36.39◦, corresponding to the lattice planes (1 0 0), (0 0 2),and (1 0 1) respectively The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036–1451)[26].

From the diffraction pattern it's obvious that the growth is dominated in these directions and these diffraction peaks can be assigned to the wurtzite hexagonal-shaped ZnO. The lattice constants a and c was determined as a = 3.228 A°, c = 5.272 A° by using the following equation [27] by the relation:

$$\frac{1}{d^2_{(h\,k\,l)}} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}. \quad (1)$$

The grain size [28] is calculated using Scherer's equation:

$$D = 0.9\lambda/(\beta\ cos\theta) \quad (2)$$

Where D: the grain size, λ = 1.5406A°, β: the Full Width Half Maximum (FWHM) , θ :the diffraction angle. Because of the heat treatment process, the thick film undergoes dislocations in its structure. The dislocation density is calculated by the equation [29].

$$\delta = 1/D^2 \quad (3)$$

Where δ is the dislocation density

Finally for reaction time 72 h were appeared the new growth at 2θ value 21.44◦,and disappeared growth lattice plane 31.96◦obvious that the growth is dominated in these new directions structure forward new lattice plane. These directions and these diffraction peaks cannot be assigned to the wurtzite hexagonal-shaped ZnO. The dislocation density was proportion with the peak relative intensity so that observed for 100% relative intensity has a maximum value for this process conditions. The structural parameters estimated and illustrated in table 1.

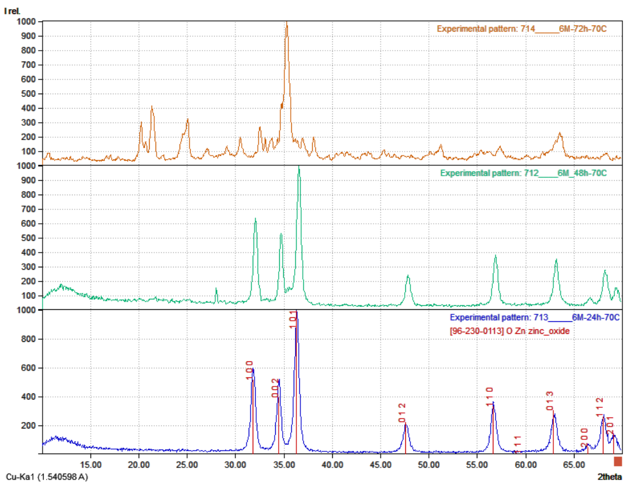


FIG. 1: XRD PATTERN OF ZnO NANOSTRUCTURES: (A) ARRAYS AS-PREPARED AT 70^{o} C FOR 24 (B) AS-PREPARED AT 70^{o} C FOR 48 H (C) AS-PREPARED AT 70^{o} C FOR 72 H

TABLE 1
THE ESTIMATED STRUCTURAL PARAMETERS OF MAJOR PEAKS (a = 3.228 Å, c = 5.272 Å) 6M (NaOH) at 70^{o} C.

6M 24 h 70 ^{o}c							
Peak No.	**Lattice plane**	**2θ (Deg)**	**FWHM (radian)**	**Int.%**	**d(h k l) (A°)**	**Grain size (nm)**	**Dislocation density δ x10^{15} ($line^2/m^2$)**
1	(100)	31.960	0.531	61	2.798	14.66	4.65
2	(002)	34.619	0.484	50	2.589	16.19	3.8
3	(101)	36.445	0.551	100	2.463	14.29	4.89
6M 48 h 70 ^{o}c							
Peak No.	**Lattice plane**	**2θ (Deg)**	**FWHM (radian)**	**Int.%**	**d(h k l) (A°)**	**Grain size (nm)**	**Dislocation density δ x10^{15} ($line^2/m^2$)**
1	(100)	32.030	0.455	61	2.792	17.1	3.415
2	(002)	34.730	0.431	50	2.581	18.1	3.021
3	(101)	36.550	0.509	100	2.456	15.4	4.171
6M 72 h 70 ^{o}c							
Peak No.	**Lattice plane**	**2θ (Deg)**	**FWHM (radian)**	**Int.%**	**d(h k l) (A°)**	**Grain size (nm)**	**Dislocation density δ x10^{15}($line^2/m^2$)**
1	(100)	21.440	0.494	40	4.141	15.4	4.20
2	(002)	34.680	0.347	29	2.585	22.5	1.95
3	(101)	35.306	0.606	100	2.540	12.9	5.95

AFM examined reported that the average grain size were 113,80,and 97 nm for samples prepare for 24,48,and 72 h respectively figure 2 appeared the granularity cumulating distributions charts. The cumulating distribution report of scan probe microscope (SPM) for the grains diameters of the sample indicate high percentage less than 100 nm excepted the sample prepare for 24 h.

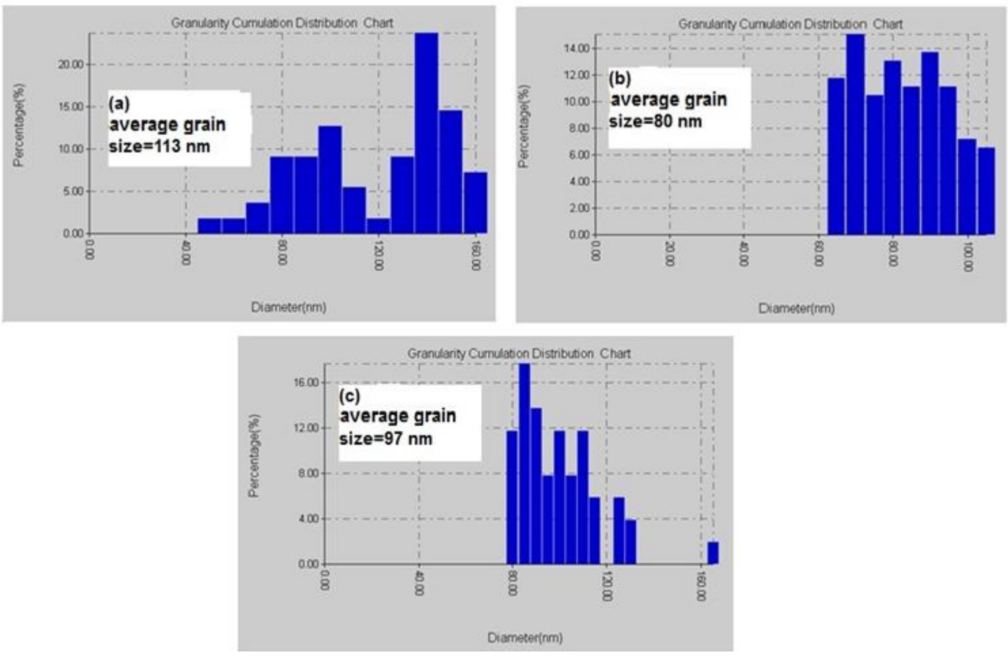
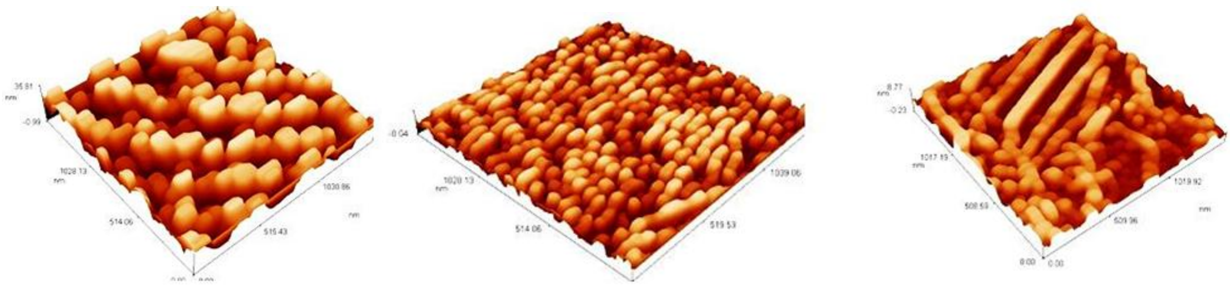


FIG. 2: GRANULARITY CUMULATING DISTRIBUTIONS CHARTS IMAGES OF THE ZnO NANO STRUCTURE HYDROTHERMALLY GROWN FROM (1G) OF ZnO NANOPARTICLES AND (6M) NaOH AQUEOUS AT 70^{o} C for (a) 24 h, (b)48 h and (c) 72 h

Figure 3 shows the AFM images of the morphology of the surface of ZnO thick film in three dimensions of the samples prepared at 70^{o} C for 24 h, 48 h, and 72 h. The surface roughness SA and peak to peak roughness for the prepared films are showing in figure 4.



(A) (B) (C)

FIG. 3 AFM IMAGES OF THE ZnO NANO STRUCTURED HYDROTHERMALLY GROWN FROM (1g) of ZnO NANOPARTICLES AND (6M) NaOH AQUEOUS AT 70^{O} C for (a) 24 h, (b)48 h and (c)72 h

At first glance it seems that the best result have a good features was a sample that prepared with reaction time 24 h, but we cannot be considered as the optimal outcome due to the fact that structured which is to be nano structured (more than 100nm) because the features of micro dimension balk is different completely with nano dimensions therefore it is to be the best sample recorded at the prepared condition at 48 h.

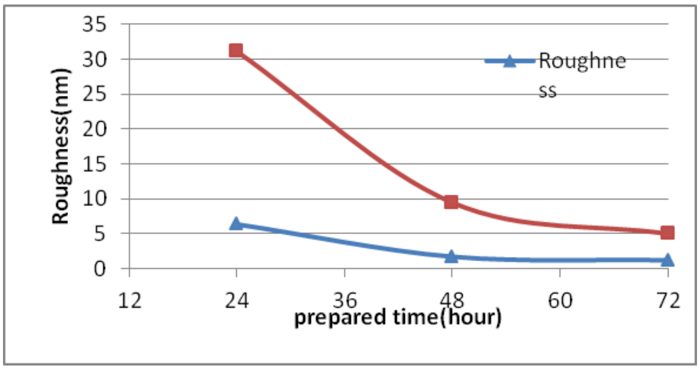


FIG.4 THE SURFACE ROUGHNESS AND PEAK TO PEAK ROUGHNESS OF OF THE ZnO NANO STRUCTURED HYDROTHERMALLY GROWN FROM (1g) OF ZnO NANOPARTICLES AND (6M) NaOH AQUEOUS AT 70^{O}C

The FE-SEM over view image of ZnO nanostructures of 1 g ZnO nanoparticles and 6M of NaOH with different growth time 24, 48 and 72 hour are shown in figures 5 a , 5b and 5c respectively at 70 oC. Its appear that the lettuce leaf structure grown with reaction time 24 hour and if taken more time for reaction it was formed the nanotubes structure with average wall thickness 30-70 nm and finally the nanosticks structures formed when the reaction time was 72h .The results were agreement with the interpreted the nano structures formed depends on the reaction time and deposition condition such as the temperature, pressure and concentrations [25]

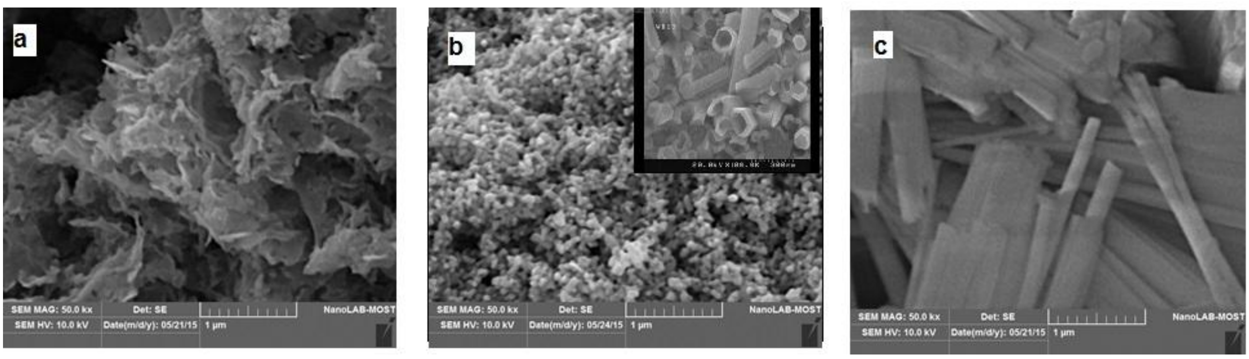


FIG. 5 THE SEM IMAGES OF THE ZnO NANO STRUCTURED HYDROTHERMALLY GROWN FROM 1 g of ZnO NANOPARTICLES AND (6M) NaOH AQUEOUS AT 70^{o}C for (a) 24 h APPEAR LETTUCE LEAF STRUCTURE, (b) 48h APPEAR NANOTUBES AND (c) 72 h APPEAR NANOSTICKS

The estimated structure parameters was found closed to typical results also dislocation density was estimated and depend on the reaction condition such as reaction time and the temperature.

IV. CONCLUSION

ZnO nano structures synthesis with hydrothermal technique is simple and efficient and it is receiving a lot of attention of late. The nanostructures are opening new applications such as nanodevices. The results presented in this article demonstrated that the effected of the parameters deal with that growth temperature. ZnO lettuce leaf can be grown in solution and changed to nanotube shape by increasing the growth reacting time during the growth process.

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