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ZnO Nanowires Growth on ZnO Seed layer deposited on FTO Glass and Study its properties and Prepared ZnO Nanowires (p-n) junction

Marwa Bakour*

Department of Physics Science, University of Aleppo, Syria

***Corresponding author:** Marwa Bakour, Department of Physics Science, University of Aleppo, Syria, E-Mail: marwabakour89@gmail.com

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Abstract

A simple and not expensive method was used for growth ZnO nanowires arrays on a thin film of ZnO as seed layer was deposited on Transparent glass substrates (FTO) by Sol-Gel method . The structural properties of these films were studied using (XRD), the structure of films that annealed at different temperatures were studied before and after the growth nanowires arrays. Seed layer film annealed at 130 °C and 300 °C were amorphs , after the nanowires growth, a one-dimension crystallization along the c-axis direction . The optical properties of these films were studied using a UV-VIS spectrophotometer, where seed layer films heat treated were studied at different temperatures. The film was re-studied after the growth of zinc oxide nanowires. Electronic transitions were obtained by doing fitting between theoretical and experimental UV VIS spectra of (FTO+ZnO) using Mathcad program. AFM images were taken after the growth process. The temperature of the annealed showed a clear effect on the growth

***Keywords:** C-Axis ZnO Nanowire arrays; Seed layer; Sol-Gel ; AFM images ; UV spectra; electronic*

Introduction

Zinc oxide is a wide direct band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), a hexagonal crystal structure , exhibiting near UV light emission, transparent conductivity, and piezoelectricity, has received much attention due to its potential applications in the optoelectronic field. One- dimensional ZnO nanostructures such as nanowires have been extensively studied for other applications including solar cells, ultraviolet (UV) light-emitting diodes, photonic crystals and transparent electrodes. The nanoscale ZnO can be growth in several forms, ZnO Nanotube,ZnO Nanorods,ZnO Nanobelt, ZnO Nanowall and ZnO Nanowires.

Several methods have been demonstrated to fabricate one-dimensional ZnO nanostructures, such as vapor liquid solid epitaxy (VLSE), chemical vapor deposition (CVD), and pulse laser deposition (PLD), but these techniques still have some limitations for substrate size and the need for high temperature operation.

Recently, the growth of ZnO nanowires in phase solutions at low temperature (below 100 °C) was reported by using the hydrothermal process , the growth had been on glass , silicon wafer and plastic substrates. This method shows that the shape of the ZnO nanowires was sensitive to the orientation of Si substrate *via* the use of ZnO nanoparticles as a seed layer. However, systematic research on the influence of quality characteristics of ZnO sol-gel thin films on the growth of ZnO nanowire arrays via hydrothermal method has rarely been reported. In this work, ZnO Nanowires will be growth by new method called Upturned crystalline growth method [1].

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Experimental details

Preparing transparent conducting fluoride tin oxide (FTO)
Microscopic slices were cleaned using $K_2Cr_2O_7$, then it's emerge diluted fluoric acid (HF) for 10 minutes for scratch external surface of Microscopic slices. After that Microscopic slice were heated put on electrical oven to 500°C. $SnCl_2.2H_2O$ (5 gr) solved in 20 ml of Ethylenglycol and sprayed on Microscopic slices several times each 5 min. The deposited resistance film SnO_2 measured and its (30) Ω (Figure 1).

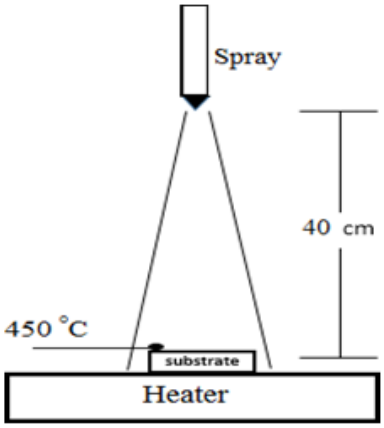

Figure 1: The deposited resistance film SnO2 measured and its (30) Ω.

Preparation ZnO Seed layer films

The ZnO thin films served as the seed layers were deposited on FTO glass substrates by a sol-gel method [22]. A coating solution contained zinc acetate dehydrate (Zn(CH3COO)22H2O, Merck, 99.5% purity) and equivalent molar monoethanolamine (MEA) (NH2CH2CH2OH, Merck, 99.5% purity) dissolved in 2- methoxyethanol (2MOE) , (CH3OCH2CH2OH, Merck, 99.5% purity). The concentration of zinc acetate was chosen to be 0.5 mol/L. The resulting solution was then stirred at 60 °C for 2 h to yield a homogeneous solution, which served as the coating solution after being cooled to room temperature. Then the solution was coated onto FTO glass substrates by a spin coater at the rate of 1000 rpm for 30 s at room temperature. Subsequently, the films were preheated for 10 min to remove the residual solvent. Then the layer film were annealed in a furnace at different temperatures ranging from 130 to 600 °C for 2 h [2].

Upturned crystalline growth method

After uniformly coating the FTO glass substrates with ZnO thin films, hydrothermal growth of ZnO nanowire arrays was achieved by suspending these ZnO seed-coated substrates upside down in a glass beaker filled with solution of 50 mM zinc nitrate hexahydrate ($Zn(NO_3)_26H_2O$, 98% purity) and 50 mM hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$, 99.5% purity).(A special device is designed to carry the sample above the surface of the solution, which is a rotatable part of the micrometer scale, which can control the height of the sample above the surface of the solution and installs below the micrometer Teflon piece can be easily rotated so that the film is fixed on the Teflon piece flat then install the micrometer on a carrier) (Figure 2).

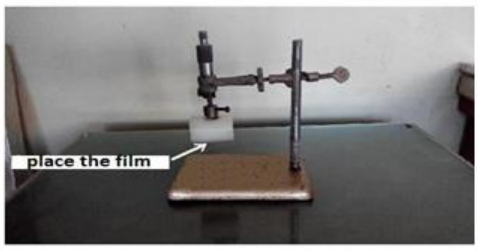

Figure 2: The crystal phase and crystallinity were analyzed at room temperature by XRD using Cu *K* radiation .

During the growth, the glass beaker was heated with a laboratory oven maintained at 60 °C for 12 h. At the end of the growth period, the substrates were removed from the solution, then immediately rinsed with de-ionized water to remove any residual salt from the surface, and dried in air at room temperature. The general morphologies of the ZnO nanowire arrays were examined by Atomic Form Microscope (AFM) [3].

Results and Discussion

Surface morphology

This shows the AFM images for the surface morphologies of ZnO nanowire arrays at different annealing temperatures of the thin films. It is notable that the ZnO nanowire arrays on the ZnO thin films annealed at 130 °C are well aligned vertically and the well defined crystallographic planes, providing a strong evidence that the nanowire arrays orientate along the c-axis. As the annealing temperatures of the ZnO thin films increase from 130 to 600 °C, the diameters of the ZnO nanowire arrays increase from 10 to 100 nm in average.The reason may be that the high annealing temperature evidently increase the interaction among the grains and leads the grains to merge together to form bigger ZnO seeds, and thus increases the diameter of the ZnO nanowires. Thus, the high (length) decreases from 500 nm to 200 nm (Figure 3).

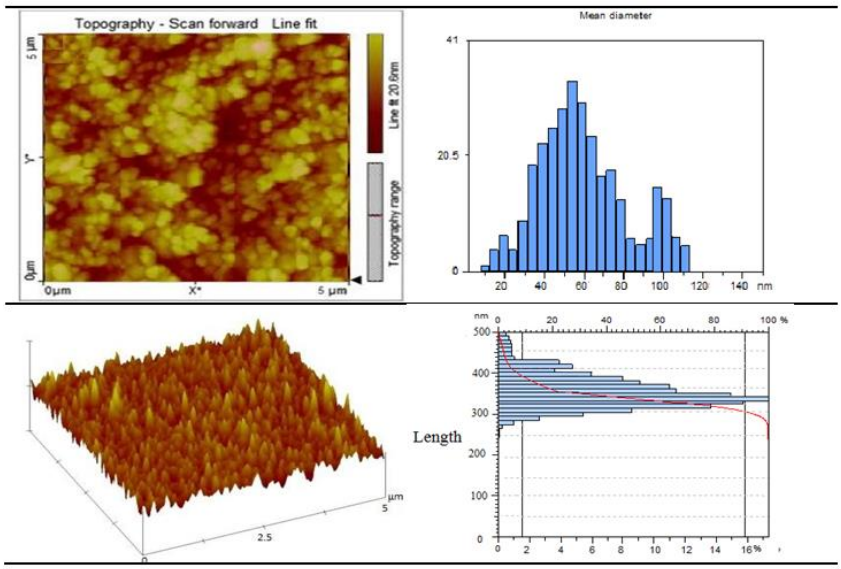

Figure 3(a): AFM image of the treated sample at 130 ^{o}C with mean diameter and length diagrams of the wires.

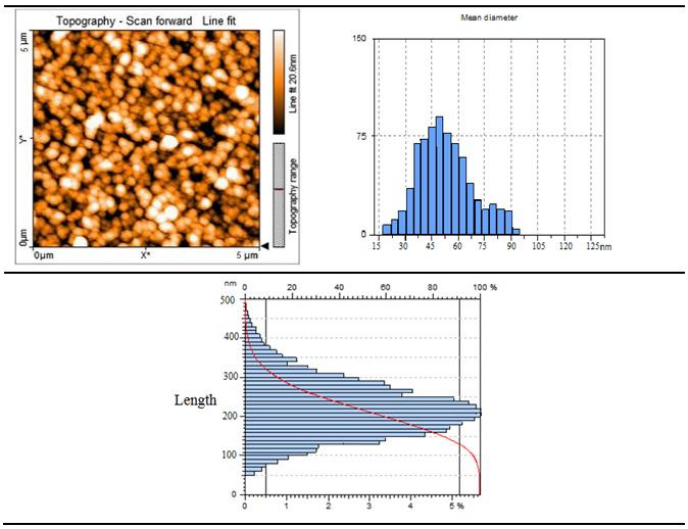

Figure 3(b) : AFM image of the treated sample at 300 ^{o}C with mean diameter and length diagrams of the wires.

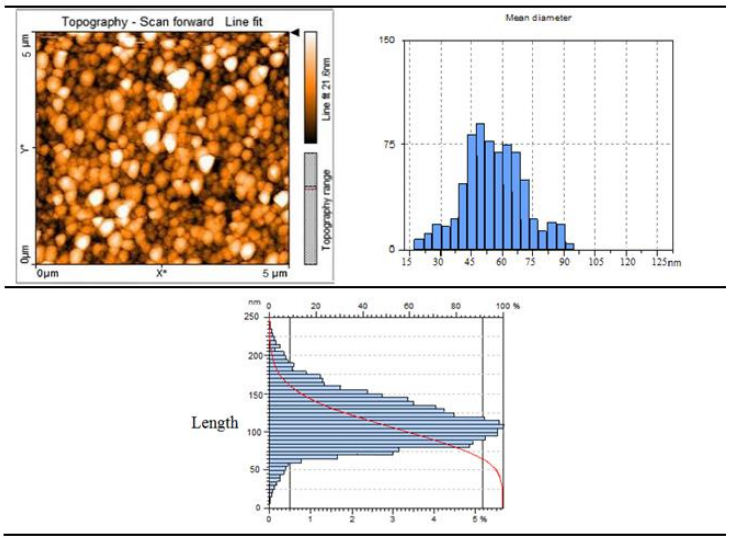

Figure 3(c): AFM image of the treated sample at 600 ^{o}C with mean diameter and length diagrams of the wires.

Structure Properties

(ZnO seed layer) :gives the XRD patterns of those ZnO thin films annealed at 130, 300 and 600 °C, respectively.The XRD patterns reveal that the (002) peak intensity varies with annealing temperature. When the ZnO thin films are annealed at 130 °C, there is no preferred (002) c-axis orientation.Where only peaks returning to the FTO appeared. At the temperature of 600 °C, (002) ,(100),(101),(102),(200) and (110) diffraction peaks corresponding to the ZnO wurtzite structure are observed in the XRD pattern (Figure 4).

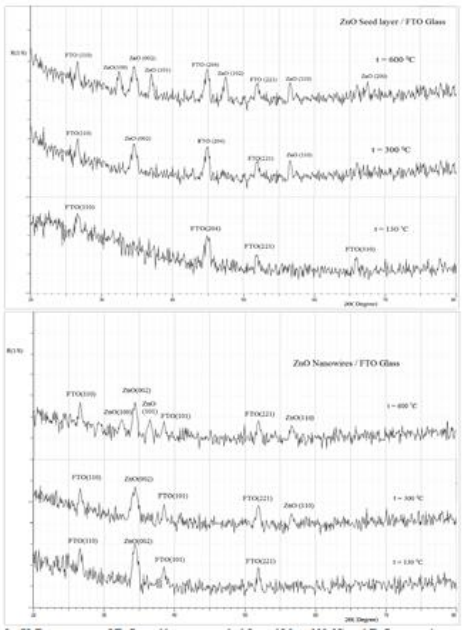

Figure 4: X-Ray spectra of ZnO seed layers annealed from 130 to 600 °C and ZnO nanowire arrays.

(ZnO Nanowires) :shows the XRD patterns of the ZnO nanowire arrays . At the temperatures of 130 and 300 °C, only a very strong (002) diffraction peak and a very weak (110) peak are observed at 300 °C , indicating that the two ZnO samples are both of high c-axis orientation. It is noticeable that for the sample annealed at 130 °C the XRD pattern shows only the (002) diffraction peak. In addition, the intensity of (002) diffraction peak is strongest, compared to other samples annealed at higher temperatures. This implies its perfect c-axis orientation. On the other hand, for the sample annealed at 600 °C, the (002) diffraction peak becomes weak, and appear other (ZnO) diffraction peaks, indicating its tendency toward random orientation (Figure 5).

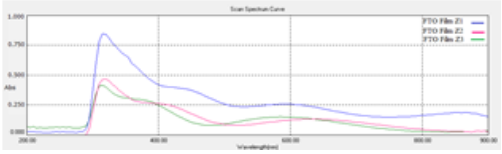

Figure 5(a) : UV spectra of FTO films.

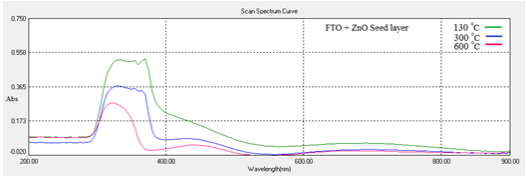

Figure 5(b): UV spectra of ZnO seed layer films annealing at 130, 300 and 600 °C.

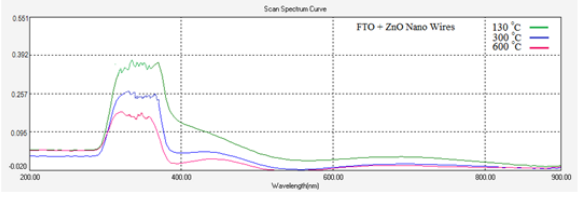

Figure 5(c) : UV spectra of ZnO Nanowires.

Reason may be that the use of (HMTA) solvent Low evaporation degree in the growth solution, indicating that the solution evaporates and stuck to the film surface in the form of vertical wires from ZnO with traces of Hexa methylene

tetraamine (HMTA).

Electronic Characteristics

The Mathcad program was used to study the electronic properties of the absorption spectrum of the treated film at 130 °C. The experimental spectrum values of the program are represented by the line with the black dots Using the Gaussian profile, the theoretical values of the spectrum are obtained. These values are adjusted until the theoretical spectrum is fully applied (100%) to the experimental spectrum [4], It determines accurate wavelength values at each absorption peak. From the accurate wavelength value of the first peak in the theoretical spectrum is 258 nm, which corresponds to 4.81 eV, which corresponds to the electronic transition due to FTO from to the eV (EC-0.61) energy level. represents the first Brillouin region in the valence band, and also the second peak at 282 nm wavelength corresponds to (4.39 eV) for the electronic transition ( ) from the third Brillouin region of the valence band to the first Brillouin region in the conduction band, also due to the FTO [13], five other ZnO transitions were obtained from the valence band to the Conductivity band. Figure 4(b) shows change in the electronic transitions and consequently a change in the electronic structure of the film after growth of ZnO Nanowire arrays due to the change of the structure of the material (Figure 6).

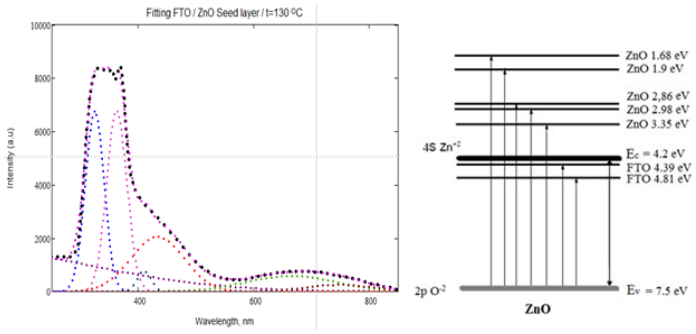

Figure 6(a): Fitting function of experimental and theoretical UV spectrum of a (FTO+ZnO Seed layer) film and possible electronic transitions.

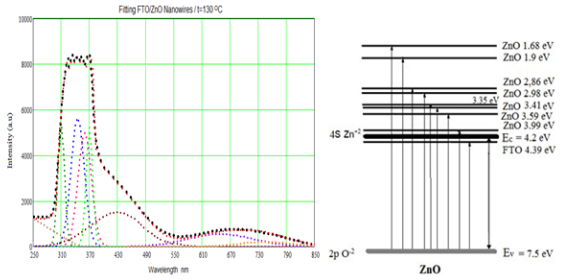

Figure 6(b): Fitting function of experimental and theoretical UV spectrum of (FTO+ZnO Nanowires) film and possible electronic transition**.**

Impedance Spectrum (IS)

Impedance spectrum was measured Using GAIN PHASE ANALYZER device type Schlumberger-SI1253 and resistance Rd

$$Z(\omega) = R(\omega) + jX(\omega)$$

Note that the spectrum of the seed layer is semi-circles, which means that the material is uniformly granulated and that the impedance increases in value as the temperature of the treatment increases. Consequently, but spectrum of nanowires is not a regular semi-circles based on Debye's theory the material is not granulated (Figure 7).

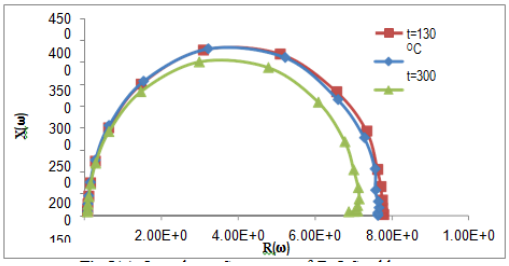

Figure 7(a): Impedance Spectrums of ZnO Seed laye.

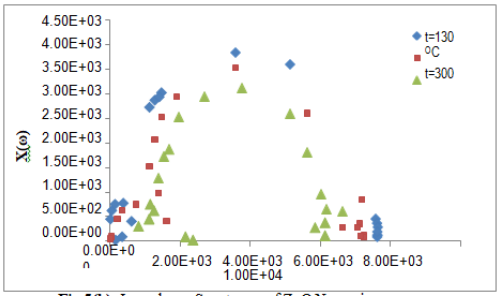

Figure 7(b): Impedance Spectrums of ZnO Nanowires.

This shows that as a result of applying a weight to the nanowires, voltage increases significantly more when applying low weights [5]. This explains that when a vertical force is applied to wires, the electrons distributed along the wire move in the same direction as the force to the lower electrode to pass current into the external circuit and produce an output potential that useful in the application of electronic devices (Figure 8).

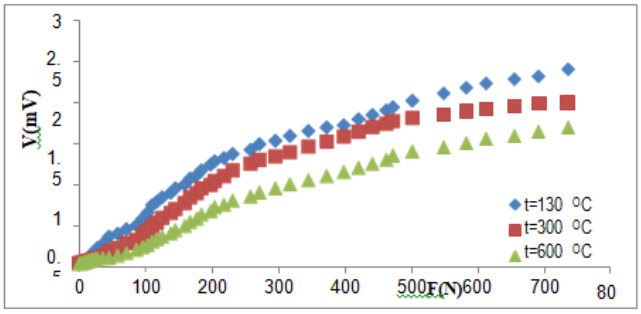

Figure 8: Output voltage when applying vertical force on ZnO Nanowires.

Piezoelectric coefficients were calculated from (Cp-F) diagram of the films that annealing at 130, 300 °C (Figures 9 and 10).

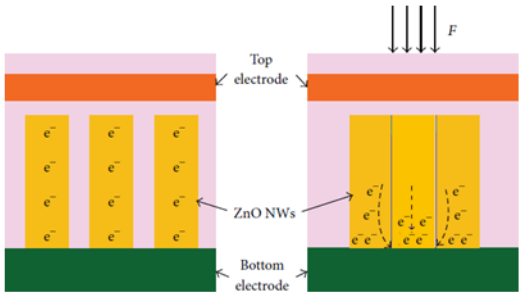

Figure 9: Effect of applying vertical force on nanowires.

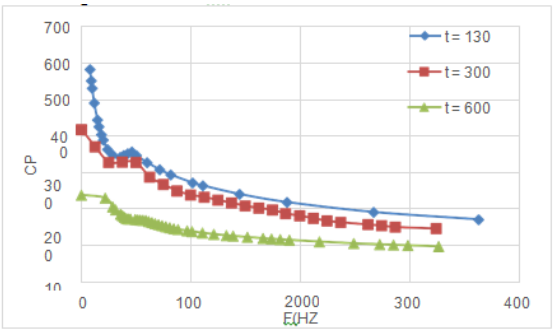

Figure 10: (Cp –F) diagrams of ZnO nanowires.

Where ( ) Electrical permittivity , (k) Electromechanical bonding factor, (y) Constant flexibility, (d) piezoelectric coefficient (Table 1).

Tabel 1: Piezoelectric coefficients of ZnO Nanowiers.

Sample				
130 ^{o}C	4.8606	0.431694	411.6376	3.72869
300 ^{o}C	5.36271	0.094369	406.0515	1.93921

Prepared ZnO Nanowires (p-n) junction

The nanowires are growth using the Upturned crystalline method using growth solution (n-type) for 4 hours, then the same sample is growth followed by a growth solution (p-type) for 2 hours. Where growth solution(p-type) prepared from zinc nitrate and HMTA and add impurity phosphorus atoms by adding phosphoric acid to solution by percentage (0.01).

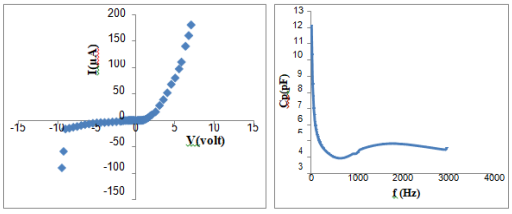

Figure 9: (I-V) and (Cp-F) curves of ZnO Nanowires (p-n) junction.

Conclusions

- Method used in growth ZnO Nanowire arrays in this work, is good and has shown results comparable to previous researches, but it simple less expensive.
- The results of XRD and AFM showed that the nanowires grew in a vertical direction for the films that were processed at

low temperatures below 300 ºC The size of the granules in the seed layer increases as the processing temperature increases and the diameter of the nanowires increases. The best growth of nanowires was for the treated film at 130 ºC.

- The electronic properties of the material vary after the growth of ZnO nanowires.
- The impedance spectrum of ZnO Nanowire arrays is not semi-circles based on Debye's theory .
- ZnO Nanowire arrays have piezoelectric properties that useful for many applications 6- ZnO Nanowires (p-n) junction have good electric properties.

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