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Annealing Influence on the Optical Properties of Nano ZnO

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ABSTRACT

Using a vacuumed spray method, Zinc Oxide has been synthesized in a vacuum at a room temperature with different thicknesses. Absorbance and transparency have been studied as a function of wavelength variation before and after annealing the samples. Peaks have occurred at different wavelengths. Energy gap variation of the same samples has been examined with wavelength variation, Eg has been dramatically reduced as wavelength increased, its best value was 1.95 eV at 700 nm. Annealing has no abrupt change on energy gap.

Key words: ZnO thin films, nano, optical properties and annealing effects

INTRODUCTION

ZnO thin film is one of the II-IV compound semiconductors and is composed of hexagonal wurtzite crystal structure. ZnO thin film presents investigating optical, acoustical and electrical properties which meet extent applications in the field of electronics, optoelectronics devices such as solar cells and sensors. ZnO thin films are applied to the transparent conductive films and the solar cells window because of high optical transmittance in the visible region at the electromagnetic wave spectrum. Studies on the application of ZnO thin films to the surface acoustic wave devices and film bulk acoustic resonator filters are being made , because of its excellent piezoelectric properties [1,2] . In addition to these properties the high thermal and chemical stability of ZnO allows using it at different environmental conditions. The efficiency and performance of any optical and electrical nanodevices are directly determined by the properties of underlying nanostructures, which are in turn greatly dependent on the crystallographic orientation, size, shape and morphology [3].
As a good candidate ZnO nanostructured films has a large excitation binding energy of 60mV at room temperature that provides more efficient excitonic lasing mechanism. The efficiency and performance of any optical and electrical nanodevices are directly determined by the properties of underlying nanostucures, which are in turn greatly dependent on the crystallographic orientation, size, shape and morphology. A highly transparent ZnO films have been prepared by many different deposition techniques and their deposition parameters play an important role in controlling the morphology and physical properties of the nanostructures. Both physical deposition , including thermal evaporation , sputtering , spray pyrolysis , metal organic chemical vapour deposition , pulsed laser deposition , molecular beam epitaxy, and chemical synthesis routes , including hydrothermal , solvo-thermal ,sol-gel electrochemical , chemical bath deposition [3] have successfully employed to prepare a wide variety of ZnO nanostructure . The physical deposition routes have the advantages of producing high quality materials but also the disadvantages of the need of high deposition temperatures. So, temperature plays a very important role in the performance of the ZnO devices.
The spray pyrolysis deposition of ZnO thin films is a technique that has been widely used for a long time in the deposition of several applications. Several types of photovoltaic cells have been produced by this method combining ZnO with different semiconductors such as CdTe and $CuInSe_2$ [4].Deposition method consists of spraying an ionic solution, containing elements of the compound material to be deposited, onto the appropriate substrate .The solution reaches the hot substrate in the form of small droplets where they are decomposed, the elements react and they are deposited the thin film.

EXPERIMENTAL DETAILS

The chemical spray pyrolysis deposition system is a local made aperture which consists of a metal cuboids box with a transparent glass door to monitor the spraying operation, and contain a holder to carry a cylindrical vase placed where solvents sedimentation occurs. This vessel have a valve to control the amount of solution flowing to slot spraying .At the bottom of the pot there is a tube surrounded by a room air spindle shape relate to slot side associated tube to enter the gas spray and also can be used for heating the sample. The whole system is exhausted by using a motor as shown in fig. 1. Sample weights were obtained by using an electronic balance (Denver Instruments), a magnetic stirrer was used to mix the solution.

Optical properties such as transmittance and absorbance were obtained using a UV- VIS spectrometer (SHIMADZU –UV 1650 PC) fig. 2. the examined wavelength region was ranged between (100-700) nm. The band gap was obtained from analyzing the optical spectrum with the absorption coefficient (α) and the photon energy (hγ) [5] using the relation -

$$A = [k\,(h\gamma - Eg)\,h/2]\,/h\gamma \qquad (1)$$

Where k is constant and n is a constant which equal to 1 for a direct band gap material, and 4 for an indirect band gap material.

ZnO diluted with ethanol were deposited 200^0 C for four samples, the mixture was left for 24 hours for homogeneity and deposition times were used as a function to get different thicknesses. Layer thickness measurements were obtained from a direct measurements difference and by weight monitoring (Denver Instrument). Deposition temperatures for all samples were 200^0 C; samples were left to cool down. Optical properties then measured at room temperature, then, annealing samples to 250,300,340 and 400^0 C respectively. Optical properties after annealing measured using the same equipment.

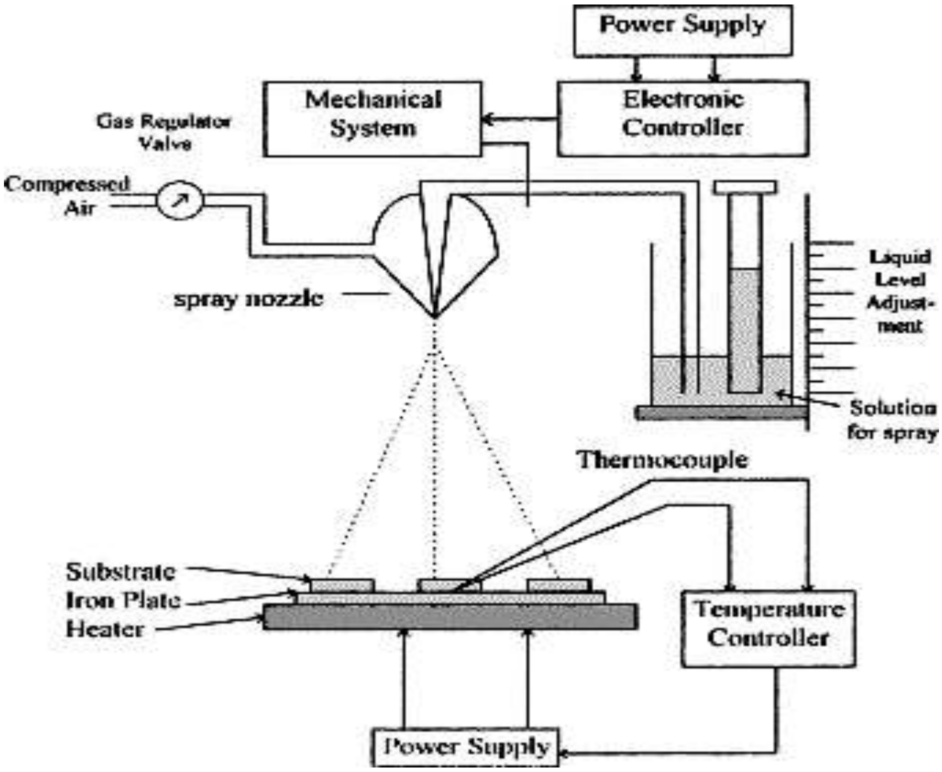

Fig. 1 Schematic diagram for the deposition system

Fig. 2 UV-Visible Spectrometer

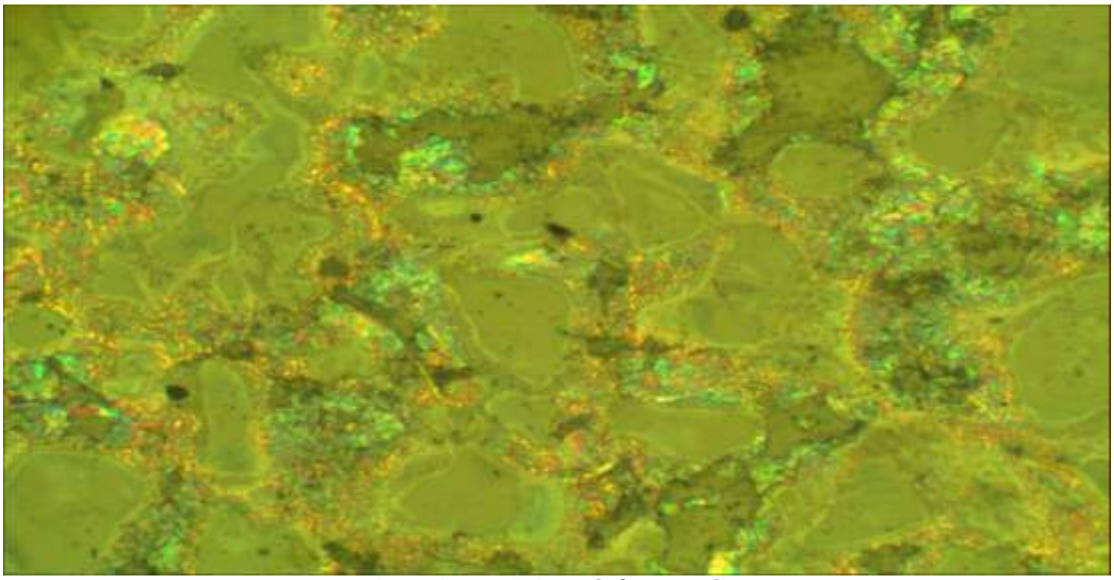

Fig. 3 Microscopic image before annealing

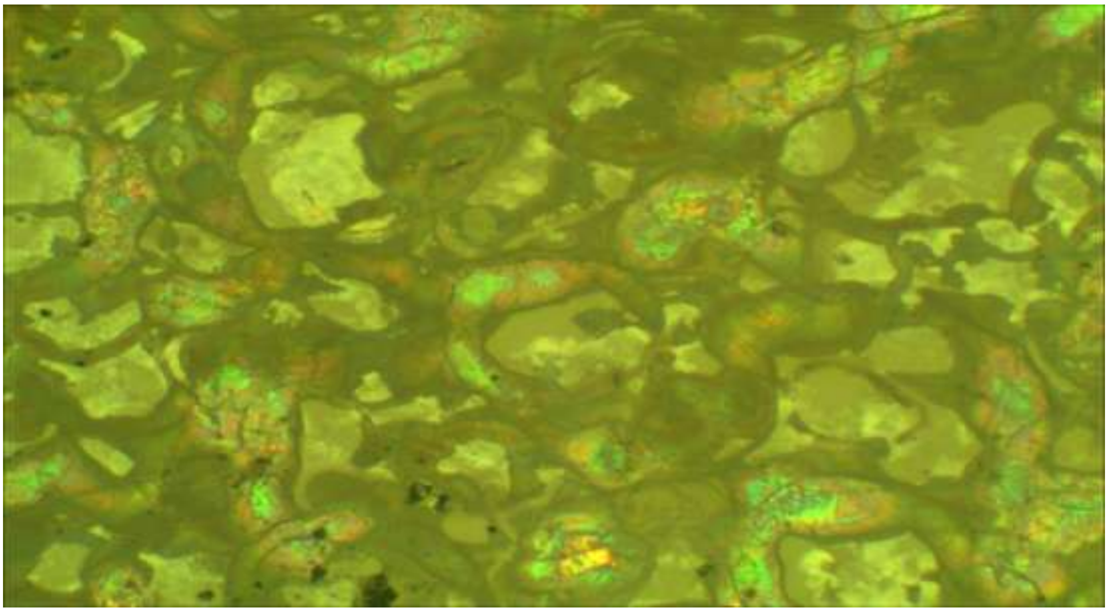

Fig. 4 Microscopic image after annealing

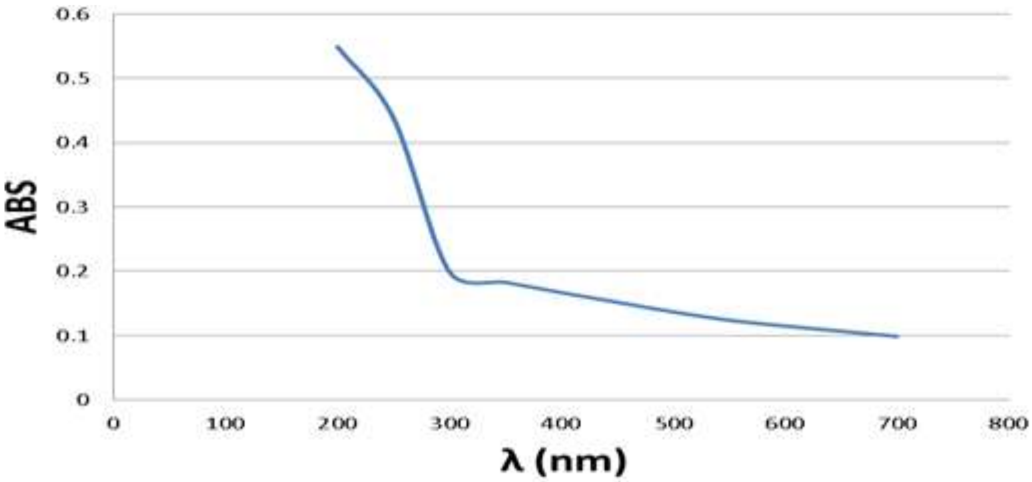

Fig. 5 Absorption spectrum before annealing

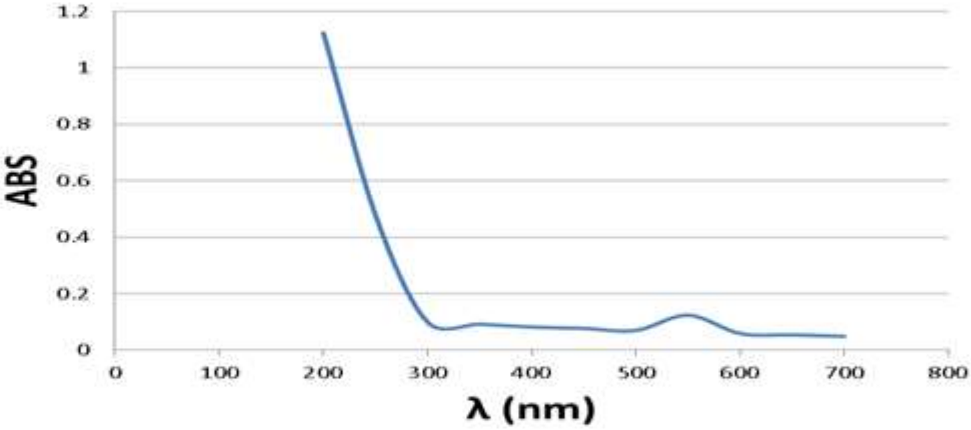

Fig.6 Absorption spectrum after annealing

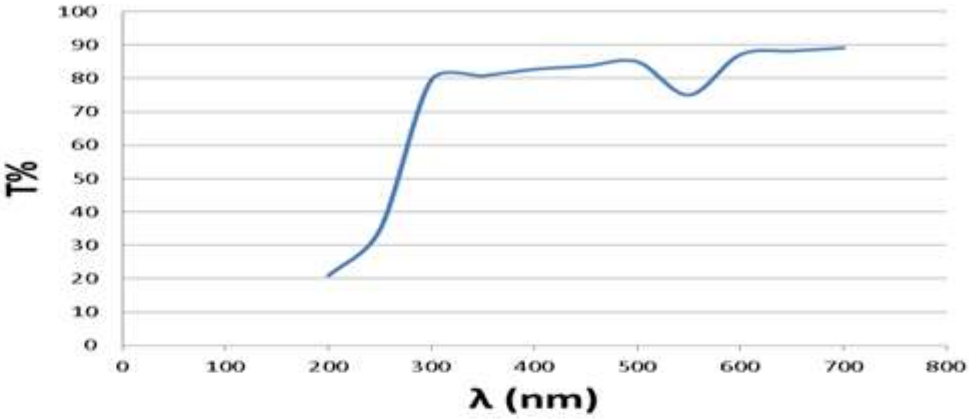

Fig. 7 Transmittance spectrum before annealing

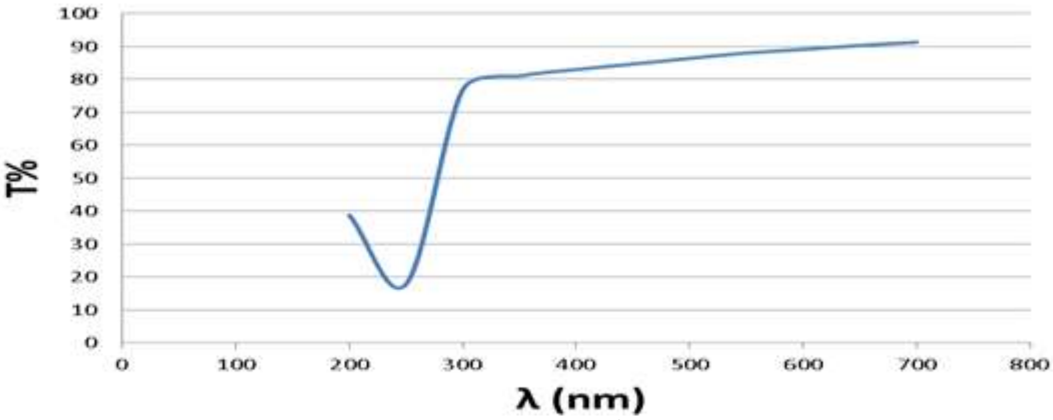

Fig. 8 Transmittance spectrum after annealing

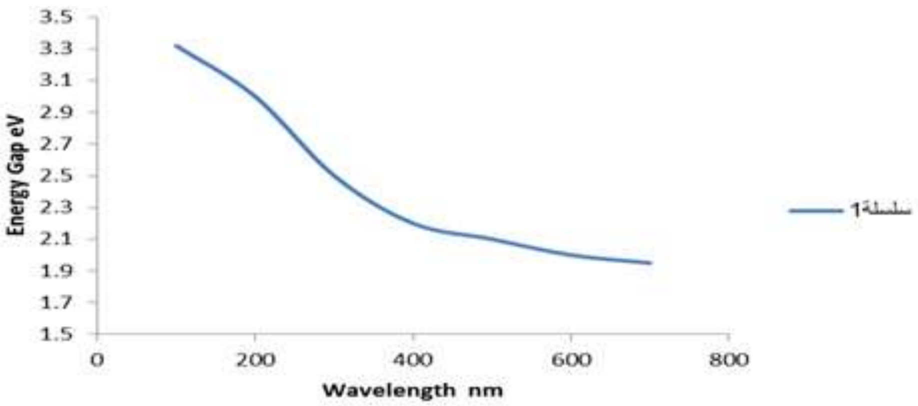

Fig. 9 Energy gap variation with wavelength

RESULTS AND DISCUSSION

Microscopic images have shown that annealing process has enhanced effects on the formation of nanostructure network of ZnO. Figures (2-3) show the microscopic structure before and after annealing. Temperature can be considered as an enhancing parameter for getting a homogenous formation; this result is in good agreement with others [6]. Absorption spectrum analysis before and after annealing are shown in figures [5-6], it is clear from the figure that a low absorption values are obtained at wavelengths >300 nm. Transmittance spectrum before and after annealing are shown in figures (7-8), in a good agreement with the absorbance spectrum , where their summation should be almost constant , transmittance values reaches a certain high values at nearly the same wavelength (i.e. >300 nm). From these figures it seems that annealing has straightened the spectrum through the visible region.

Using values calculated from equation (1), energy gap has plotted against wavelength, fig. (9) Shows this variation. Eg has decreased dramatically as wavelength increases, its best value was 1.95 eV at a wavelength of 700 nm. This result can be explained in terms of Burstein –Moss effect [7, 8, 9], according to the shift of Fermi level and block some of the lowest states.

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