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SYNTHESIS AND STUDY OF ZnO NANORODS AND Fe-DOPED ZnO NANOFLOWERS BY ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION (APCVD) TECHNIQUE

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ABSTRACT

In this study, undoped zinc oxide nanorods and Fe-doped zinc oxide nanoflowers, were successfully prepared by atmospheric pressure chemical vapor deposition (APCVD) technique via using aqueous solution of zinc acetate [$(ZnCH_3COO)_2.2H_2O$] without any catalyst. The dopant source for the Fe-doped nanoflowers was the aqueous solution of iron (III) nitrate [$Fe(NO_3)_3{\cdot}9H_2O$]. The undoped zinc oxide nanorods and Fe-doped zinc oxide nanoflowers were deposited on glass substrates at 550 and 500 ^oC substrate temperatures respectively inside reactor of APCVD system. X-ray diffraction (XRD) measurements for all samples reveal a highly (002) oriented crystalline structure. Scanning electron microscopy (SEM) results illustrated that all nanostructures are nanorods and nanoflowers. Size of the nano grains were investigated by SEM results and XRD measurements. Energy dispersive X-ray spectroscopy (EDS) showed that all structures contain Zn and O elements for undoped ZnO and Fe for doping state. AFM analysis showed that the surface grains of the Fe-doped samples are homogeneous with less RMS roughness values compared with the as-grown undoped ZnO samples.

Keywords: ZnO, Nanostructures, nanorods, nanoflowers, APCVD.

I. INTRODUCTION

Wide-gap semiconductor materials with nanostructures, such as nanorods, and nanowires, have attracted great interest due to their importance in both scientific research and potential technological applications. Zinc oxide is one such wide-gap (ZnO) compound II-VI semiconductor. Doped and undoped ZnO thin films are currently under intense investigation and development for optoelectronic. To date, much work has been focused on nanostructured ZnO due to its potential applications in numerous areas such as nanoscale electronics and photonics [1]. Zinc oxide (ZnO) is an n-type semiconductor with both wide band gap (3.37 eV) and large exciton binding energy of 60 meV with a hexagonal wurtzite structure, which finds applications in ultra-violet/blue emission devices, laser diodes, solar cells and in acoustic devices [2].

A variety of methods have been employed for the synthesis of ZnO nanomaterials, such as high-temperature vapour-liquid-solid or thermal evaporation processes. In those processes, either high vacuum and temperature or some catalysts such as gold nanoparticles are required. Recently, aqueous solution deposition approaches based on wet chemical and bottom-up processes have been reported to synthesize ZnO nanorods and there are several deposition techniques that have been employed to grow undoped and doped ZnO thin films like chemical vapor deposition (CVD), magnetron sputtering, pulsed laser deposition (PLD), sol-gel process and spray pyrolysis (SP) [3,4]. Doping is a widely used method to improve the electrical and optical properties of semiconductors. However, synthesis route is also very important to get different types of nanostructures with different properties [5]. The control of the particle shape is one main concern for nanostructured material synthesis because electrical and optical properties of nanomaterials depend sensitively on both size and shape of the particles. Therefore, it is desired to synthesize nano-material in a controllable shape and size by a simple approach [6]. The aim of the present work is preparation and investigation of the growth of undoped and Fe-doped ZnO nanostructure by APCVD system via using solution method.

II. EXPERIMENTAL

Undoped and 4% Fe-doped ZnO thin films are prepared by atmospheric pressure chemical vapor deposition (APCVD) technique. The base material in the preparation of undoped zinc oxide thin films was zinc acetate dehydrate [$Zn(CH_3COO)_2H_2O$] (high purity 99.96%, supplied by B.D.H. Laboratory chemicals group, Poole England) which was dissolved in distilled water to obtain an aqueous solution at 0.5 M concentration, then put into evaporation unit. The dopant source of iron is the aqueous solution of 0.5 M of iron (III) nitrate [$Fe(NO_3)_3{\cdot}9H_2O$]. Glass substrates were cleaned first by putting them in ultrasonic bath which contains (TCE) solution for 10 min and then washed in acetone, and methanol for the same period and lastly washed by distilled water and dried by hot air.

APCVD system consists of quartz tube furnace opened from two ends (Reactor) and operates under atmospheric pressure. Its interior diameter is 5.5 cm and its length is 60 cm. The ends are closed by rubber plugs, one of them is used as inlet for the vapor from evaporation unit through a narrow glass tube and the other is used as outlet for the gases and to enter the narrow glass tube which contains the thermocouple (K-type). The vapor of liquid is transferred with O_2 as carrier gas (1 L/min) into a heated quartz tube furnace where the glass substrate of (2 x 2.5 cm^2) area are placed on 10^o inclined holder then set up for a growth time of (25 min) as shown in Fig. (1).

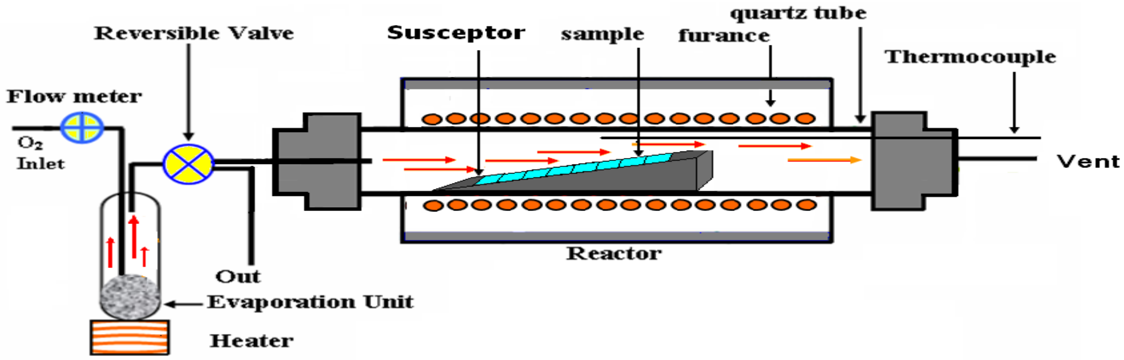

Fig. 1: Schematic diagram of APCVD system

The growth temperatures of ZnO nanostructures in the quartz tube furnace were 550 and 500 ^oC for the undoped and Fe-doped samples respectively. The shapes of the ZnO nanostructures were observed by using scanning electron microscope (JEOL JSM-6380) and EDS attached with it and atomic force microscope (model AAA3000 supplied by Angstrom Advanced Inc.). Films thickness is measured by gravimetric method and found to be 500 nm and 400 nm for nanorods and nanoflowers respectively. The X-ray diffracttion (XRD) data of the films were taken using a SHIMADZU (XRD-6000) diffractometer with CuKα radiation of 1.5406 Å wavelength. All identifications for ZnO and iron oxide phases are in agreement with (JCPDS card No.36-1451) and (JCPDS card No.33-0664) respectively.

III. RESULTS AND DISCUSSION

The morphologies of the as-grown ZnO nanorods were investigated using scanning electron microscopy (SEM). As shown in Fig. (2). Entangled ZnO nanorods were grown on the glass substrate at 550 °C with preferred orientation (001). According to SEM images the diameters of the nanorods are about 250 nm and their lengths reach (1.4 µm). The lattice parameters of (a) and (c) are calculated using XRD patterns for the films [7].

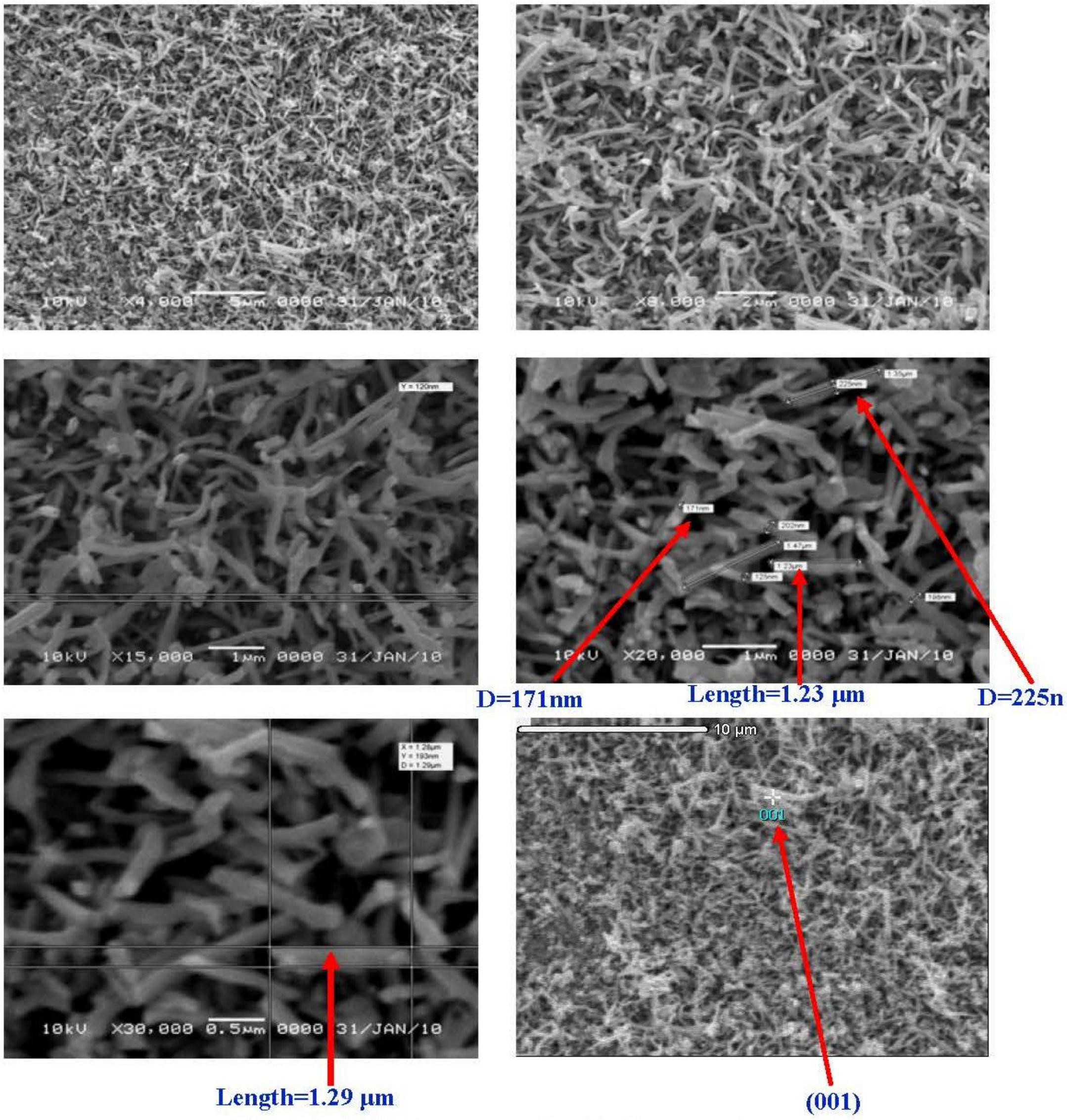

Fig. 2: SEM images of the ZnO nanorods

Fig.(3) shows the AFM image of ZnO nanorods grown on glass substrate at 550 °C. The RMS roughness value of the prepared samples was 79.5 nm for scanned area of 10x10 µm^2. This value has been verified using section line analysis.

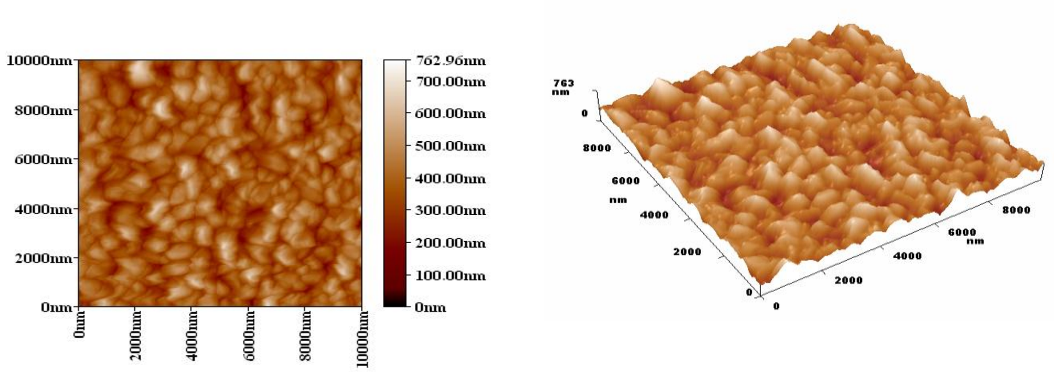

Fig. 3: AFM images of the ZnO nanorods

Fig.(4) shows the XRD pattern of ZnO nanorods. All the peaks match well with the bulk ZnO, which could be indexed as the hexagonal wurtzite structure of ZnO (a=3.2498 Å, c = 5.2066 Å, JCPDS card no. 36-1451). Furthermore, it can be seen that the (002) and (100) diffraction peaks are higher compared to the corresponding SEM images which exhibit (001) direction only as shown in Fig. (2). Table (1) shows the XRD analysis results for the ZnO nanorods prepared in this study.

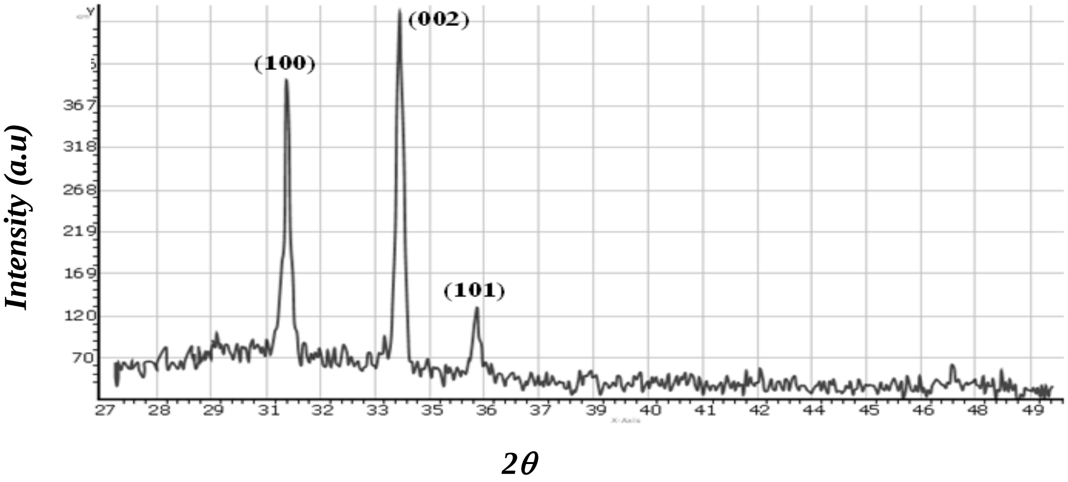

Fig. 4: XRD pattern of the ZnO nanorods

Rose-like zinc oxide nanoflowers were successfully synthesized on glass substrates via the ZnO films deposited at (500 ^{o}C) and Fe-doped ZnO at (4%) concentration. Figure (5) shows SEM images for ZnO nanoflowers grown on glass substrates. Variety of nanoflowers can be seen. These nanoflowers are composed of nanobranches and hexagonal nanosheets layer by layer which form rose-like shape and the end of any branch looks like nanorod with different diameter.

Table 1: XRD analysis for ZnO nanorods

Hkl	*(100)*	*(002)*	*(101)*	*JCPDS for ZnO (002)*
2θ	31.749	34.409	36.233	34.421
d(Å)	2.8161	2.6042	2.4772	2.6033
FWHM (deg.)	0.123	0.149	0.169	_____

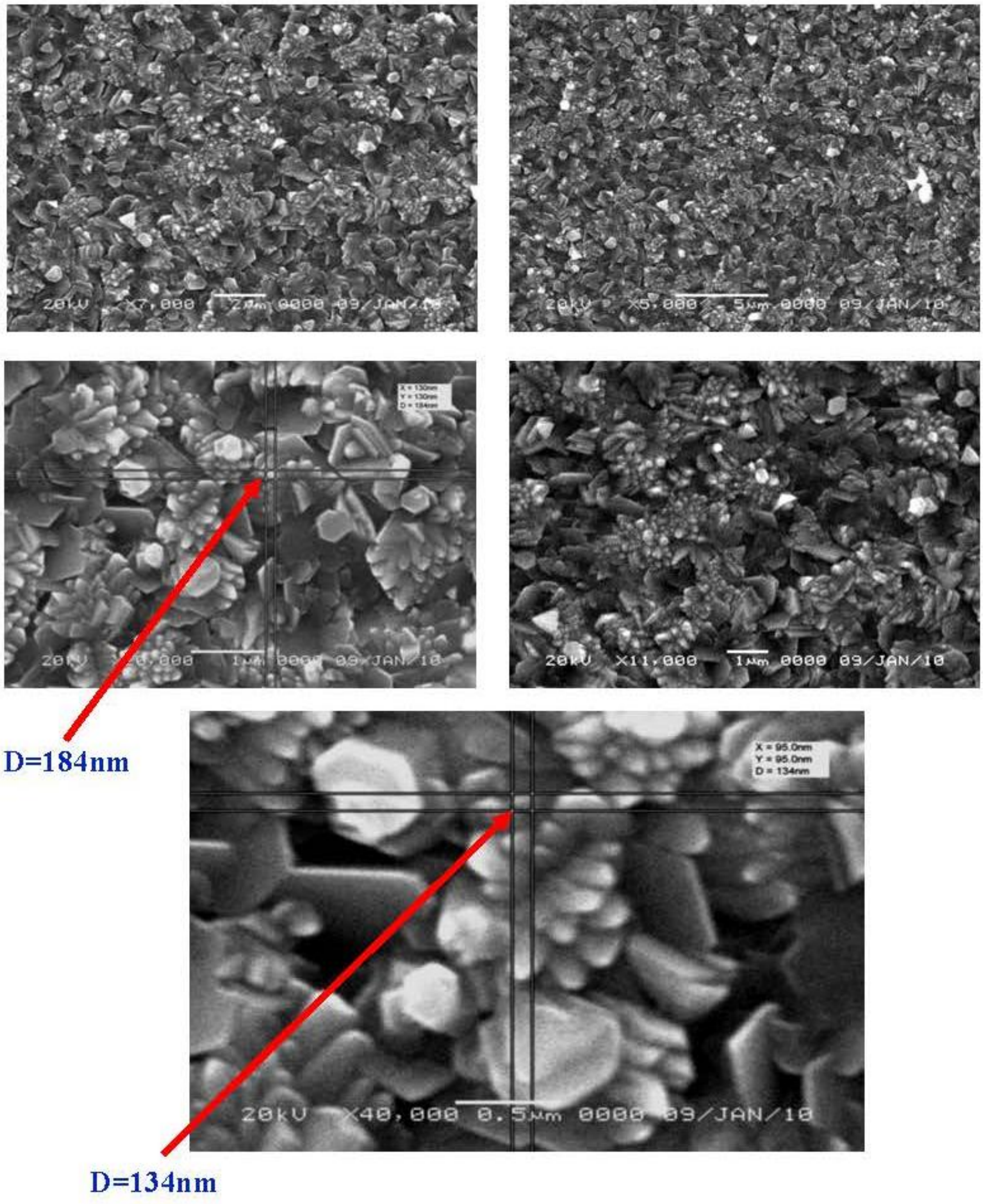

Fig. 5: SEM images of the ZnO nanoflowers.

Fig. (6) shows the AFM image of the Fe-doped ZnO at (4%) concentration. It can be seen that the surface grains are homogeneous with less RMS roughness value compared with the as-grown undoped ZnO samples. The RMS roughness value of this sample was 39 nm for scanned area of 20x20 μm^2.

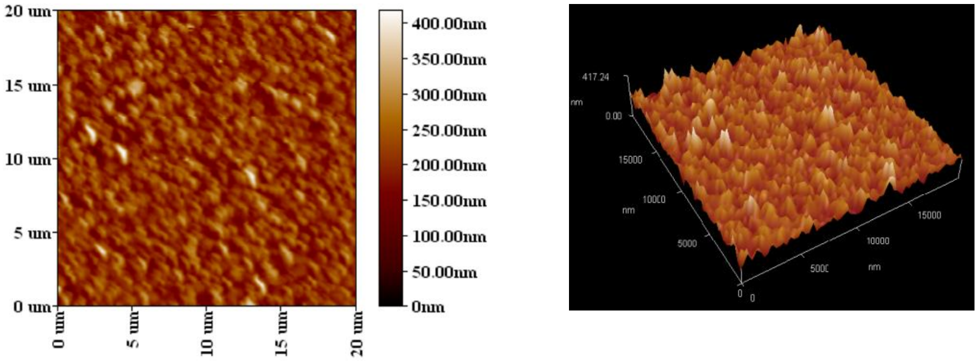

Fig. 6: AFM images of the ZnO nanoflowers.

Fig. (7) shows the XRD pattern for ZnO nanoflowers. All of the major diffraction peaks can be indexed to the wurtzite phase, which is very close to the reported data (JCPDS NO. 36-1451), only ZnO peaks were found in all the samples and absence of Fe, FeO, or Fe_2O_3 peaks within the detection limit. The high intensity of the (101) peak suggests that is the good preferred growth direction. As shown in Fig. (7) the (002), (101) and (102) peaks of the doped sample show a low shift to higher angle (2θ) due to the substitution of Zn^{2+} (74 pm) by smaller Fe^{3+} (64 pm). This is in good agreement with Linhua Xu et al [8].

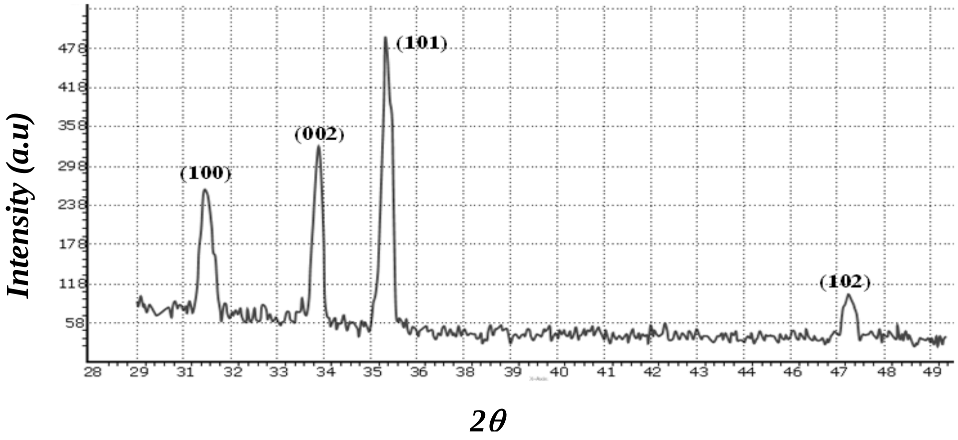

Fig. 7: XRD pattern of the ZnO nanoflowers

Table (2) shows the XRD analysis results for the ZnO nanoflowers prepared in this study. SEM images for all figures clearly show that the temperature of the substrate and doping play an important role for improving the crystallinity of the ZnO films [9], where we observe real shapes of hexagonal ZnO crystals with preferred orientation (001) and (002). Table (3) shows some of the major findings collected from the reported literature on ZnO deposited at different substrates [10-14].

Table 2: XRD analysis for ZnO nanoflowers

Hkl	*(100)*	*(002)*	*(101)*	*(102)*	*JCPDS for ZnO (002)*
2θ	31.750	34.429	36.257	47.257	34.421
d(Å)	2.8162	2.6024	2.4752	1.9101	2.6033
FWHM (deg.)	0.451	0.231	0.212	0.425	_____

Table 3: ZnO nanostructures prepared at different substrates

Structure	Material	Substrate	Diameter (D) and length by SEM	Crystallite size by Scherrer's relation
Nanorods	ZnO	Si (111)	200-400 nm	____ [10]
Nanoparticles	ZnO	glass	_____	15-18 nm [11]
Nanoparticles	ZnO	glass	250 nm	20-30 nm [12]
Nanoflowers	ZnO	Si (100)	60-200nm,4-6 μm	44 nm [13]
Nanorods	ZnO	glass	100-400 nm	_____ [14]

The reason for getting different diameters for ZnO nanostructures obtained on different substrates is attributed to the nucleation mechanism, where oxidation of Zn atoms, and growth of ZnO nanorods and nanoflowers [15]. The APCVD method is based on the formation of solid phase from the solution, which involves nucleation and growth. In the process of nucleation, the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film by heterogeneous reactions at the substrate surface. When the vapor is precipitated on the down face forms the ZnO nuclei, thus ZnO nanostructures grow from the nuclei on the substrate; however the growth for all above shapes were without any metal acting as the catalyst. EDS analysis for nanorods and nanoflowers as shown in Figures (8-a, 8-b) respectively shows that the dominant composition of ZnO, whereas the quantitative analysis of the as-deposited ZnO films shows two strong peaks corresponding to Zn (Kα, Lα) and O (Kα), which confirms the high purity of the ZnO thin film.

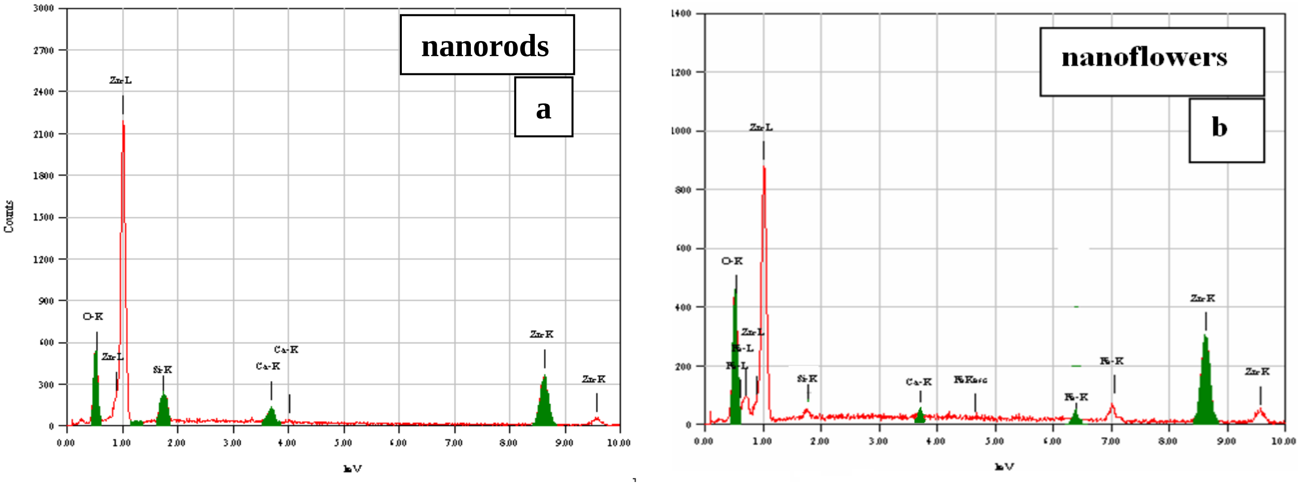

Fig. 8:: Energy dispersive spectroscopy (EDS) for ZnO nanorods (a) and nanoflowers (b)

These results also agree with Ning Zhang et al [16]. However, we observe in the doping state (nanoflowers) the appearance of Fe element as Fe (Kα, Lα) with low intensity due to low concentration. We have also detected the peaks corresponding to Si and Ca for all samples and these peaks are attributed to the glass substrate used in preparing the ZnO nanostructures in this study. AFM analysis showed that the surface grains of the Fe-doped ZnO nanoflowers are homogeneous with less RMS roughness values compared with the as-grown undoped ZnO nanorods.

IV. CONCLUSIONS

In the present work, zinc oxide nanostructures as nanorods and nanoflowers have been deposited with different substrate temperatures by atmospheric chemical vapor deposition (APCVD) technique. SEM images indicate that the films have different shapes of ZnO nanostructures. X-ray diffraction studies confirm that these nanostructures are highly crystalline and have wurtzite hexagonal structure. The substrate temperature improves crystallinity order and doping with Fe at 4% changes the structure of ZnO.

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