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Research Article

# THE EFFECTS OF THE $MN^{2+}$ IONS ON THE MORPHOLOGICAL PROPERTIES OF ZINC OXIDE THIN FILMS

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***Abstract:*** *The nanocrystalline ZnO thin films were successfully prepared via the sol-gel spin coating method for the different atomic ratios Mn doping (0.1%, 0.5%, 1%, 2%, 5%). The detailed surface analysis of samples was performed by Atomic Force Microscopy (AFM). The AFM results indicate that the ZnO films have nanostructure. The morphological characteristics of films show that Mn2+ ions are included in the crystal lattice of ZnO without changing the structure. The influence of Mn doping on film growth has resulted in an increase in fiber size and roughness. The fiber size values of the films were found to vary from 0.898 µm to 2.960 µm with Mn doping. The study revealed the possibility with Mn doping of controlling, optimizing and improving the morphology in ZnO thin-film production.*

***Keywords****: Mn-doped ZnO, Morphological analysis, Atomic force Microscopy, Microfiber, Roughness*

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## 1. Introduction

As a multifunctional material, ZnO has been known for a long time and has a wide range of uses due to its remarkable properties [1, 2]. Therefore, ZnO is a suitable material for electronic and optical devices [3]. Furthermore, ZnO offers unique photocatalytic properties [4].

The modification of the superior properties of zinc oxide by doping has been extensively investigated, but studies are still ongoing [5]. Nonetheless, the physical, optical, morphological, and electrical characteristics of ZnO nanostructures can be improved by the doping of some transition metal ions such as Cr, Mn, Fe, Co, and Ni [6, 7]. The doped metal oxide, incorporated into ZnO nanostructures, affects its bandgap, electrical and optical characteristics [8]. The contribution of metal oxides or transition metals leads to an increase in surface imperfections, which are the cause of electrical and optical conductivity [9]. These transition metal ions, especially $Mn^{2+}$-ions, are important because they are optically active and provide localized spins that interact with the spin of electrons/gaps in the host lattice [10]. Furthermore, the fact that the ionic radius of $Mn^{2+}$ (0.066 nm) is close to the ionic radius of $Zn^{2+}$ (0.060 nm) is one of the most important reasons for choosing $Mn^{2+}$-ions as a dopant [11].

Various film parameters such as thickness and homogeneity must be accurately controlled in the production of thin films to be used in different application areas [12]. The sol-gel spin coating technique offers advantages, including better stoichiometry control [13], lower process temperature [14], better homogeneity [15], low cost, the use of high purity starting materials [16], and the easy coating of large substrates [17, 18]. For these reasons, this method is one of the simplest and most effective methods of producing thin films in a controlled manner [19-21]. It is possible to use pure and Mn-doped ZnO nanostructures in optoelectronic devices that have great importance due to their optical properties. Numerous studies in this field have been conducted mostly on magnetic characteristics of Mn-doped nanostructured ZnO thin films. However, there is no study based on morphological properties in the literature.

In the present research, nanostructured doped and pure ZnO films were deposited on commercial glass substrates by employing the spin coating technique. The main objective is to examine the effects of Mn-concentration on the microstructure and optoelectrical properties of ZnO in detail. Despite the fact that a number of structural, morphological, magnetic, and optical characteristics of Mn-doped ZnO films produced by the spin coating technique have been reported in various studies, based on the surface morphology have not been encountered much in the current literature. Moreover, only a few articles report on the nonlinear optical approach of this layer based on the Mn-doped ZnO layers.

## 2. Materials and Methods

### 2.1. Materials

All chemicals used in the processes are provided by Sigma-Aldrich. 2-methoxy ethanol (CH3OCH2CH2OH) (purity 99.8%) as the solvent, and monoethanolamine (MEA) (purity ≥ 99.0%) as the stabilizer, Manganese(II) acetate tetrahydrate ((CH3CO2)2Mn.4H2O) (purity ≥ 99%) as the dopant source and zinc acetate dihydrate (Zn(CH3COO)2.2H2O) (purity 99.9%) was utilized as the starting material, and their analytical purity was maintained.

### 2.2. The preparation process of gels

Zinc acetate was doped with Manganese (II) acetate tetrahydrate at different atomic ratios (0, 0.1, 0.5, 1, 2, and 5 %) to form the sol-gel solutions of ZnO that contained Mn- at various atomic ratios. The solutions, measured as 1 M and 10 ml, were placed in a test tube containing 2-methoxy ethanol as solvent. These solutions were then stirred at room temperature using a magnetic stirrer (5 minutes at 1000 rpm) and an ultrasonic stirrer (5 minutes). This stirring process was repeated under identical conditions after adding the dopant source. After the doping, the stabilizer (monoethanolamine) was added and stirred under the same conditions. Finally, the mixture was stirred for 60 min at 60 C with a magnetic stirrer in order to obtain a homogeneous sol- from the solution,

### 2.3. Deposition of the pure and Mn-doped ZnO nanolayers

Microscope glass was used as a substrate to grow the obtained Mn: ZnO gels as a thin film layer. The microscope glasses were cleaned ultrasonically with acetone, ethyl alcohol and de-ionized water for 10 minutes, respectively. After cleaning, glasses were completely dried by using nitrogen gas. The growth of thin films on glass substrates was carried out by a spin coater (1000 rpm, 30 seconds). The above-mentioned procedure was repeated 5 times in order to obtain a homogeneous surface. For drying,

the substrates were held on a heater pre-set to 200 °C for 5 min. In the last step, the acquired films were heat-treated at a temperature of 500 °C for 60 min. Care was taken to prepare thin films under the same conditions for all the doping ratios.

### 2.4. Characterization techniques

For the purpose of examining the topographic characteristics of Mn: ZnO thin films, 2D and 3D-micrographs of the surfaces were obtained by a PARK SYSTEM XE-100E Atomic Force Microscope. The structural characteristics of the formative phases of the nanolayers were examined. In order to capture images from the nanolayers surface, a suitable cantilever and the non-contact mode was utilized. After the 40 μm x 40 μm and 5 μm x 5 μm images of Mn: ZnO thin films were obtained, the detailed morphological analysis of the scanned regions was performed on each sample surface.

## 3. Results and Discussion

### 3.1. Detailed morphological analysis of nanostructured Mn: ZnO thin films

Figs. 1(a-f) shows the 2D/3D AFM micrographs obtained at different magnifications (40 μm x 40 μm and 5 μm x 5 μm) of pure and Mn-doped ZnO film samples. From the obtained micrographs, it is determined that the surface morphology of Mn-doped ZnO films is formed in the form of nanofiber by the combination of nano-sized granules and in the form of microfiber by the combination of these nanofibers. These microfibers are uniformly dispersed, even though dense and irregular on the film surface. The size and shape of fibers change according to Mn-concentrations. As the Mn ratio increases, it is determined that the size of the microfibers formed increases in parallel with the increasing grain size. The reason for the mentioned alteration in fiber dimensions is Mn-atoms forming the intermediate position in ZnO [22]. By using AFM images, the surface roughness values ($R_q$) of thin films were computed to be 61.053, 68.384, 71.534, 123.955, 169.251, and 189.985 nm for 0, 0.1, 0.5, 1, 2, and 5% of Mn-doped ZnO samples, respectively. A linear representation of the surface roughness and cross-sectional analysis of the samples is given in Fig. 2 (a-f).

The sample with the lowest $R_q$ is pure ZnO. The increase in the size of the microfibres also increased the surface roughness value. The lower roughness value of the pure ZnO sample showed a more homogeneous distribution of small grains on the surface in terms of surface morphology. 2D-AFM images obtained at high resolution, high magnifications and line profiles of the fibers forming the morphology of the samples are shown in Figs. 3 (a-f).

The red markers in the line profiles indicate the microfiber, while the blue and green markers indicate the nanofibers that make up this microfiber. From the AFM micrographs and line profiles in Fig. 3 (a-f), it is observed that microfibers are formed by the combined growth of multiple nanofibers with the help of doping. With the addition of Mn-doping to the ZnO matrix, the structure of the fiber (Fig. 3-a) formed by nanogranules changes. These nanogranules are shaped in the form of nanofibers, and then they were changed together to form microfibers.

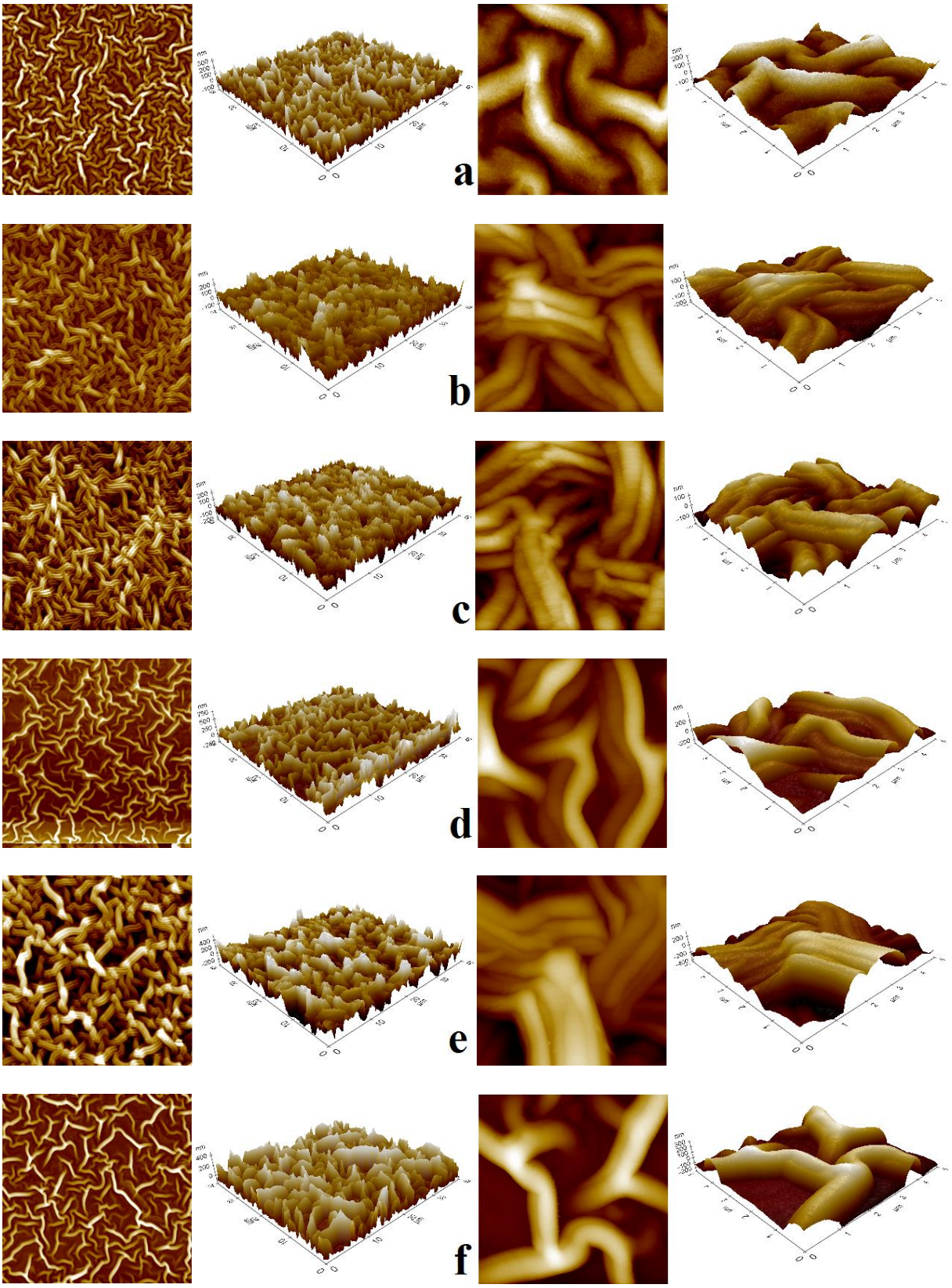


**Fig. 1.** AFM Micrographs of undoped and Mn-doped ZnO nanocrystals.
**a)** ZnO, **b)** 0.1 % Mn, **c)** 0.5 % Mn, **d)** 1 % Mn, **e)** 2 % Mn and **f)** 5 % Mn
*Left (40 µm x 40 µm) 2D/3D –view, Right (5 µm x 5 µm) 2D/3D –view*

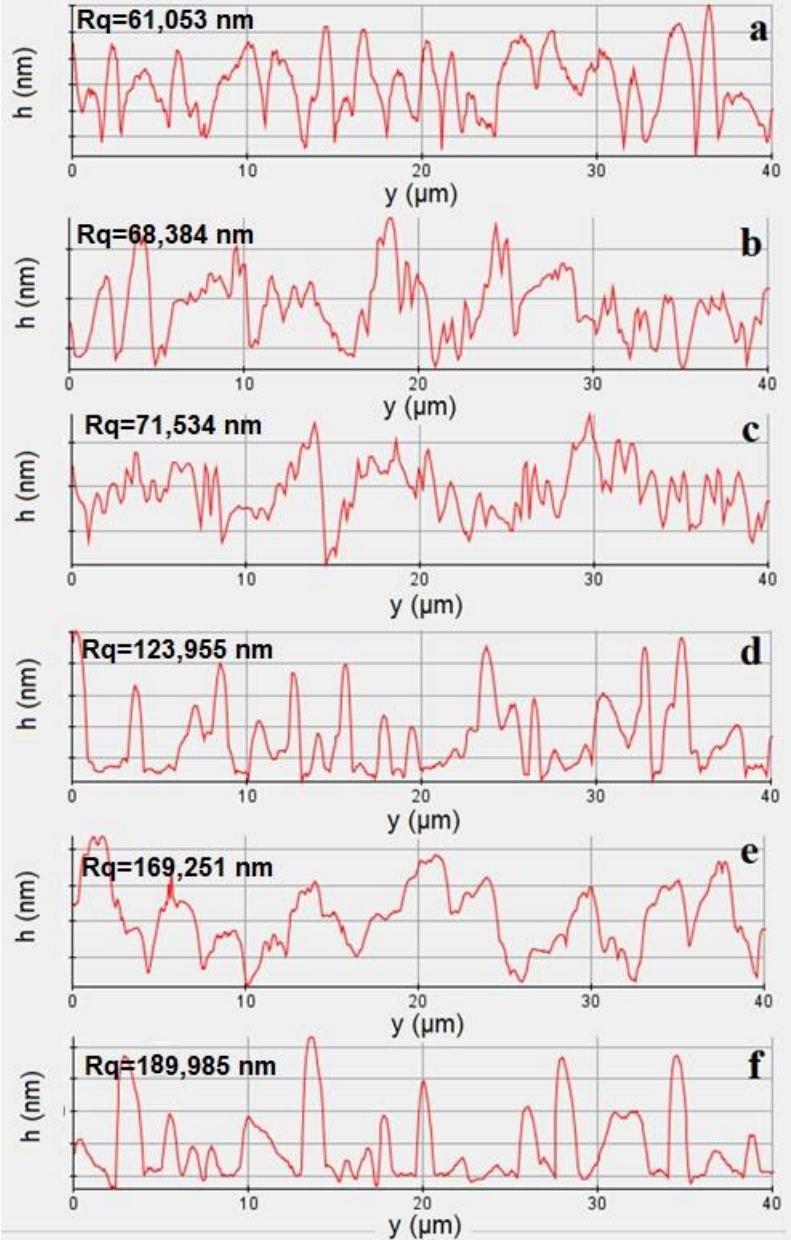


**Fig. 2.** AFM section analysis of Mn-doped ZnO thin films.
**a)** ZnO, **b)** 0.1 % Mn, **c)** 0.5 % Mn, **d)** 1 % Mn, **e)** 2 % Mn and **f)** 5 % Mn

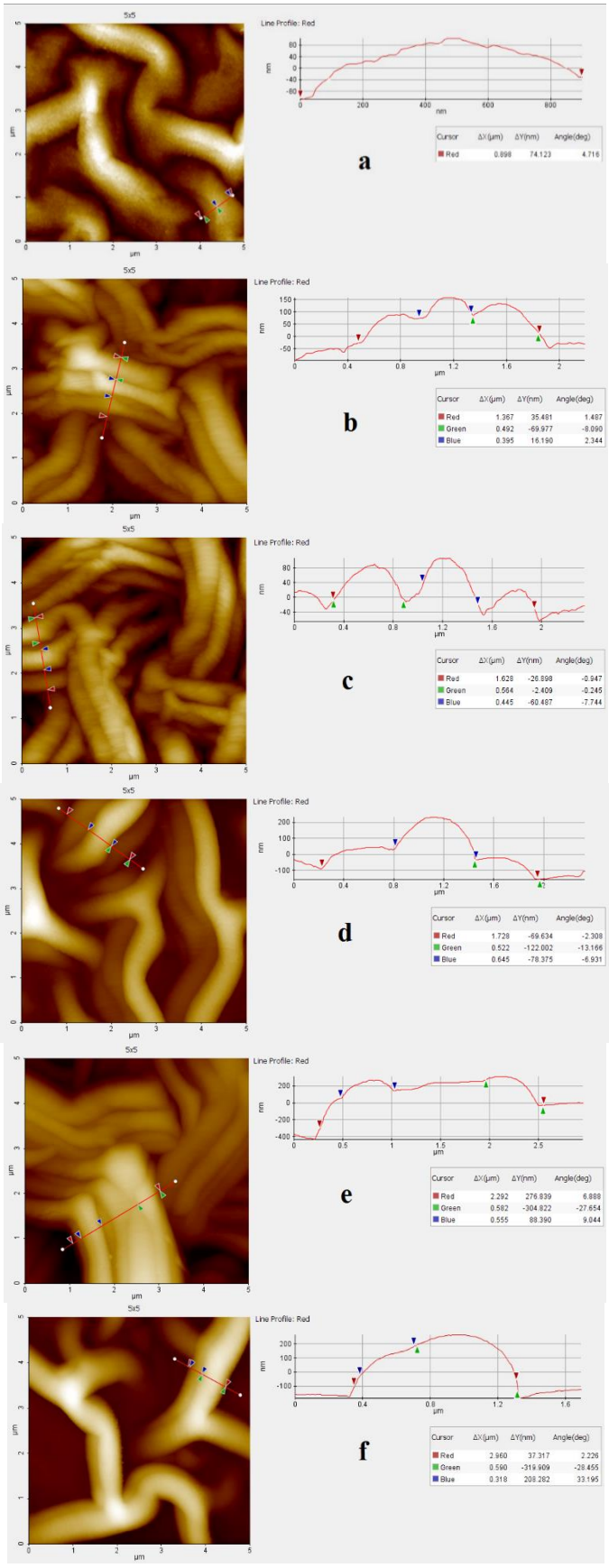


**Fig. 3.** AFM image and line profiles of ZnO fibers in samples

**a)** ZnO, **b)** 0.1 % Mn, **c)** 0.5 % Mn, **d)** 1 % Mn, **e)** 2 % Mn and **f)** 5 % Mn

The total thickness of the fibers of the samples was calculated to be 0.898, 1.367, 1.628, 1.728, 2.292, and 2.960 µm for 0, 0.1, 0.5, 1, 2, and 5% Mn-doped ZnO film samples, respectively. The variation in surface roughness and fiber size depending on manganese content is given in Fig. 4.

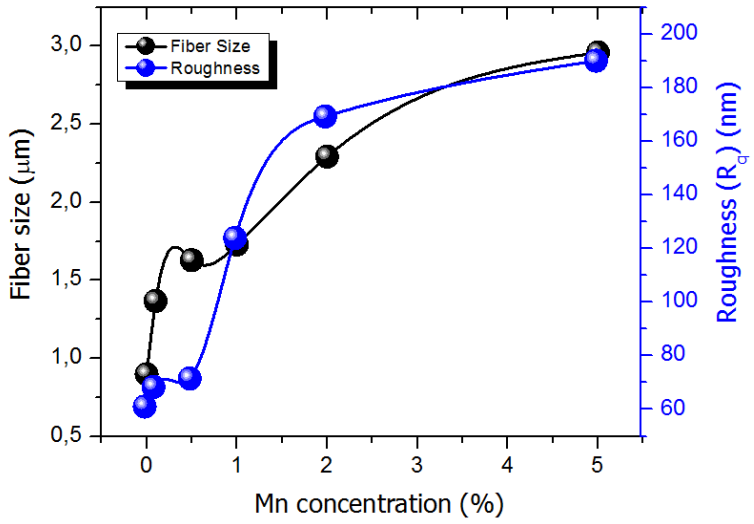


**Fig. 4.** The variation of fiber size with the Mn-content and roughness of ZnO thin films.

These nanofibers forming microfibers become thick in parallel with Mn-doping. As a result of this thickening, the size of the microfibers also increases, thereby increasing the surface roughness. The increase in surface roughness is caused by the fact that with Mn-doping, the dispersive properties of ZnO decrease [22] and the aggregation of nano-sized granules first form nanofibers, and microfibers are formed by the combination of these nanofibers. Moreover, the amount of Mn-doping causes significantly changes the surface roughness.

**Table 1.** Morphological parameters present work on ZnO nanolayers

| | ***$R_q$ (nm)*** | ***Fiber size (µm)*** |
|---|---|---|
| ***Pure ZnO*** | 61.053 | 0.898 |
| ***0.1% Mn doped ZnO*** | 68.384 | 1.367 |
| ***0.5 % Mn doped ZnO*** | 71.534 | 1.628 |
| ***1 % Mn doped ZnO*** | 123.955 | 1.728 |
| ***2 % Mn doped ZnO*** | 169.251 | 2.292 |
| ***5 % Mn doped ZnO*** | 189.985 | 2.960 |

## 4. Conclusions

Mn: ZnO thin films were successfully produced with the sol-gel spin coating technique, a simple and effective method. The impact of Mn doping concentration on the morphological properties was discussed in detail. The micrographs obtained by AFM showed that the surface morphology was in the form of microfiber consisting of nanogranules and was significantly changed by Mn doping. It was found out that, as the Mn ratio increased, fiber sizes and surface roughness increased due to the increase

in grain sizes of the films. The morphological characteristics of films state that Mn2+ ions substitute for the Zn2+ ion without altering the wurtzite structure of ZnO. All these data confirm that Mn doping alters morphological properties.

**The compliance to Research and Publication Ethics:** This work was carried out by obeying research and ethics rules.

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