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Structural Investigation of ZnO Thin Films Obtained by Annealing after Thermal Evaporation

Gökhan Utlu*[1]

Abstract

In this study, ZnO thin films, with thicknesses of 80-240 nm are prepared by thermal evaporation of ZnO pellets on glass substrates. Then, these films are annealed in air atmosphere at 300°C for 2 hours. ZnO formation has been investigated as a function of the film thickness. As deposited films appear to be brown since they are rich in Zn, whereas Zn phases are replaced by ZnO phases after annealing and the films show a transparent appearance. In thinner films (80-100 nm) the ZnO phases are not observed, but Zn phase intensities decrease after annealing. Especially when the thickness is increased in 132-240 nm thick films, ZnO phases are observed after annealing, and their intensity is increased and polycrystalline structures are formed. XRD measurements show that Zn (002), Zn (100) and Zn (101) phases are present in our films before annealing. After annealing, the intensity of these zinc peaks decreases firstly due to the film thickness, and then at ZnO (100), ZnO (002) and ZnO (101) phases are formed. SEM, AFM analyzes show that ZnOs are formed in the form of nanorods on the surface and after these anneal the columnar growths occur and the particle diameters increase.

Keywords: ZnO thin film, thermal evaporation, annealing, XRD, SEM, AFM techniques.

1. INTRODUCTION

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor. It has a high exciton binding energy of 60 meV at room temperature [1-3]. It is an important advantage that ZnO material can be produced by different methods and the structural / optical properties can be adjusted according to the desired applications, making it interesting for material science [4-5]. ZnO is also one of several optically transparent and electrically conductive metal oxide materials. Due to these superior properties, ZnO material has many applications such as gas sensors, photovoltaic devices, solar cells, piezoelectric devices, light emitting diodes, transparent conducting oxide electrodes (TCOs), UV photodetectors, spintronic devices, near UV and blue lasers [6-8]. Several methods have been used to synthesize ZnO thin films, such as spray pyrolysis, pulsed laser deposition, spraying, sol-gel, and thermal evaporation [9-10].

In this study, ZnO films were obtained by thermal evaporation of high purity ZnO particles followed by annealing in air atmosphere. Firstly, ZnO thin films, with thicknesses of 80-240 nm are prepared

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by thermal evaporation of ZnO pellets on glass substrates. Then, these films are annealed in air atmosphere at 300°C for 2 hours. ZnO formation has been investigated as a function of the film thickness, using XRD, SEM and AFM characterization techniques. Thus, in this study, the film thickness and the annealing effect at 300°C were investigated on the growth and structural properties of ZnO film.

2. EXPERIMENTAL DETAILS

In this study, firstly ZnO thin films were deposited on glass substrates by thermal evaporation of ZnO pellets of purity 99.99 % using an Edward High Vacuum Coater System with the base pressure of about $1x10^{-6}$ Torr. The glass substrates were cut into small pieces of 10 mm × 10 mm size. After then, these substrates cleaned with the standard chemical cleaning process. Prior to film deposition, a process called glow discharge under high vacuum was carried out to improve film deposition on the substrate. Then ZnO films with thicknesses ranging from 80 to 240 nm were produced by thermal evaporation on glass substrates. The thicknesses of the ZnO films were determined by a quartz crystal oscillator during the deposition.

Finally, all ZnO films were then annealed in air for two hours at 300˚C. Thickness values of the as deposited ZnO films were listed in Table1.

Table 1. Thickness values of the ZnO films

ZnO samples	Thickness (nm)	Annealing Temperature for two hours (˚C)
Sample 1	80	300
Sample 2	100	300
Sample 3	132	300
Sample 4	175	300
Sample 5	240	300

The structural investigation of the ZnO films was performed using X-Ray Diffraction (XRD), Scanning Elektron Microscopy (SEM) and Atomic Force Microscopy (AFM). Philips X'Pert Pro x-ray diffractometer with CuKα line has been used for the determination of the crystallographic phases in the XRD analyses. SEM measurements were analyzed using the Philips XL-30S FEG scanning electron microscope. AFM measurements have performed using Ambient AFM Nanomagnetics Instruments.

3. RESULT AND DISCUSSIONS

3.1 XRD analysis of the ZnO films

XRD spectra of the as-deposited and annealed ZnO thin films are shown in Figs. 1-6 as a function of the selected films of 80, 132 and 240 nm thickness.

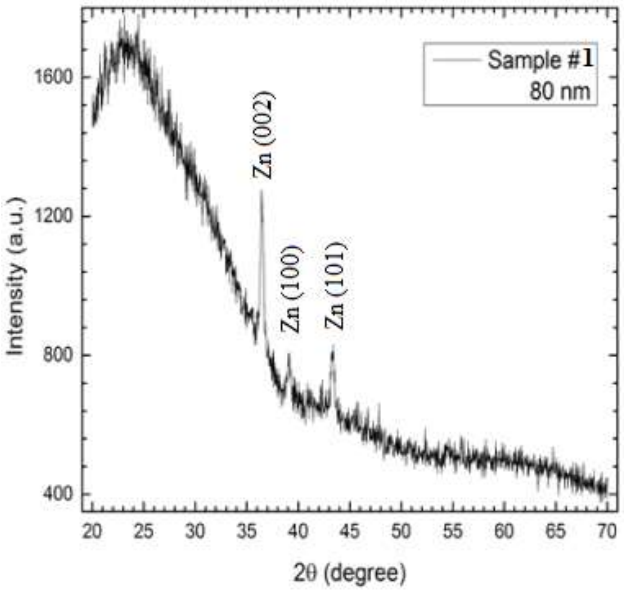


Figure 1. XRD spectra of the ZnO thin films of 80 nm (before annealing)

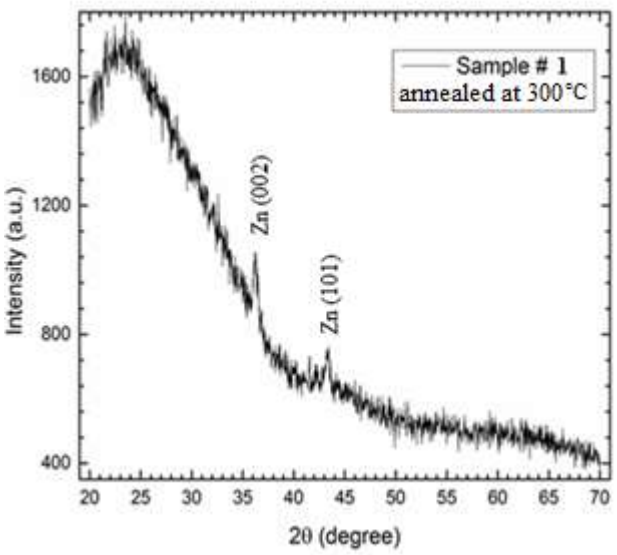


Figure 2. XRD spectra of the ZnO thin films of 80 nm (after annealing)

As it can be seen in Fig.1 as deposited sample with thicknesses of 80 nm show only Zn peaks which are observed at 2Θ ≅ 37˚, 2Θ ≅ 39˚ and 2Θ ≅ 43˚ they are Zn(002), Zn(100), Zn(101) phases, respectively. Fig.2 shows that after annealing at 300˚C, Zn phases reduction occurs.

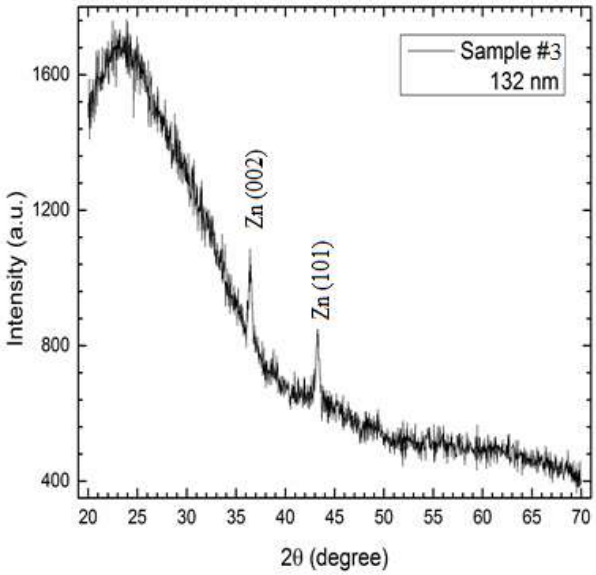


Figure 3. XRD spectra of the ZnO thin films of 132 nm (before annealing)

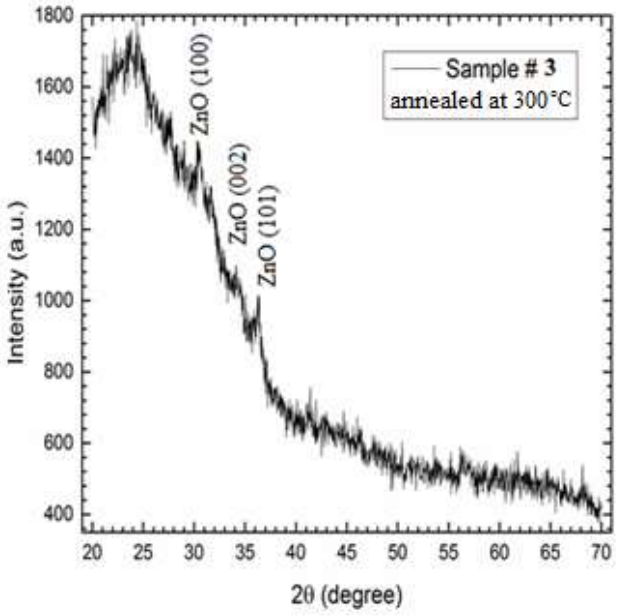


Figure 4. XRD spectra of the ZnO thin films of 132 nm (after annealing)

On the other hand, when Fig.3 and Fig.4 are examined, the oxidation behavior is observed in the annealed samples if the film thickness increases to 132 nm. Furthermore, Zn phases disappear and ZnO phases become visible; this indicates that the Zn phases replaced by ZnO.

But as the film thickness increases from 132 nm to 240 nm, after annealing process, intensities of the ZnO phase increases and sharp ZnO phases are formed. Fig5 and Fig 6 show XRD spectra of the 240 nm ZnO film before and after annealing, respectively.

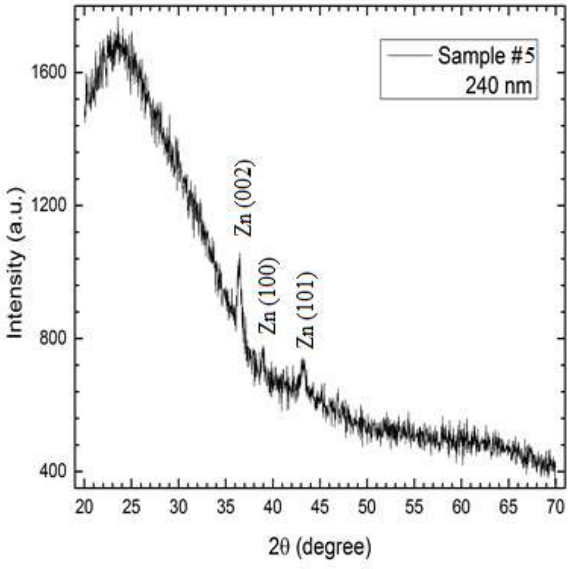


Figure 5. XRD spectra of the ZnO thin films of 240 nm (before annealing)

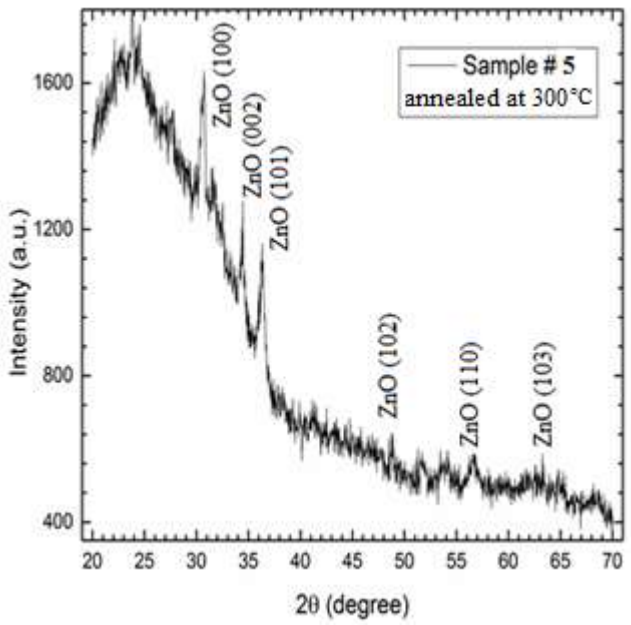


Figure 6. XRD spectra of the ZnO thin films of 240 nm (after annealing)

XRD diffraction analysis shows that as deposited films have three Zn phases correspond to the (002), (100), (101) directions. After annealing at 300˚C for two hours, Zn phases intensities decrease and also ZnO peaks appear. This indicated that Zn phase converted to ZnO phase. In thinner films (80-100 nm) the Zn phase intensities decrease and ZnO phase doesn't occur after annealing. In films with a thickness of 132-240 nm, when the thickness increases, ZnO phases are formed after annealing, their intensity increases, and polycrystalline ZnO structures occur. Therefore, many phases with zinc oxide (100), (002), (101), (102) and (110) orientations have been observed. In other production methods, most of ZnO thin films have (002) preferential orientation [3, 6, 7]. This difference may be due to changes in the growth mechanisms of ZnO. Because diffusion of oxygen in ZnO formation is very important. This is particularly dependent on composition, structure and thickness. Since all the deposited films in this study are rich in Zn, they appear brown first. Due to the entering of oxygen to the structure after the annealing, ZnO phases are formed depending on the film thickness and the films show a transparent appearance.

ZnO structures produced by thermal evaporation preferred polycrystalline orientation in accordance with the literature [7, 11, 12]. We have used thermal evaporation method and obtained ZnO thin films which have polycrystalline hexagonal wurtzite structure, in this study.

3.2 SEM analysis of the ZnO films

The SEM images obtained from ZnO films annealed at 300 °C are shown in Figs. 7-9 for the selected films of 80, 132, and 240 nm thickness values. SEM studies reveal that nanorods were formed on the surface of all ZnO films after annealing. It has been observed that these nanorods on the surface have a random distribution.

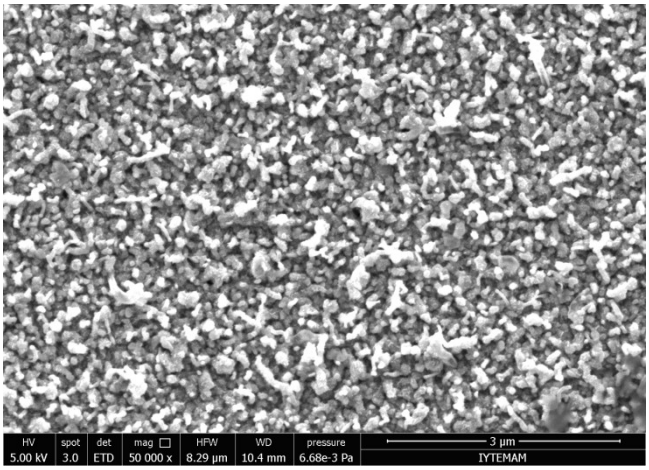


Figure 7. SEM micrographs of the ZnO films of 132 nm after annealing

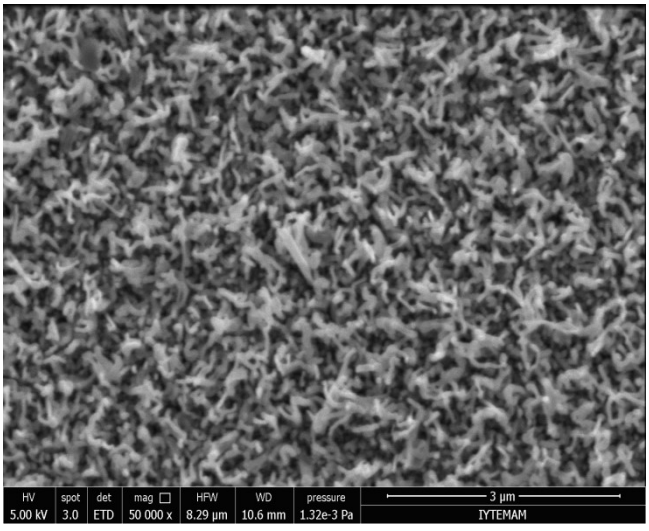


Figure 8. SEM micrographs of the ZnO films of 132 nm after annealing

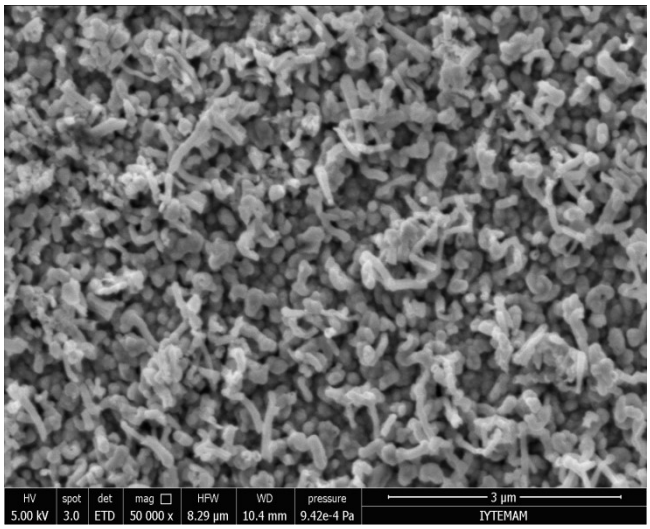
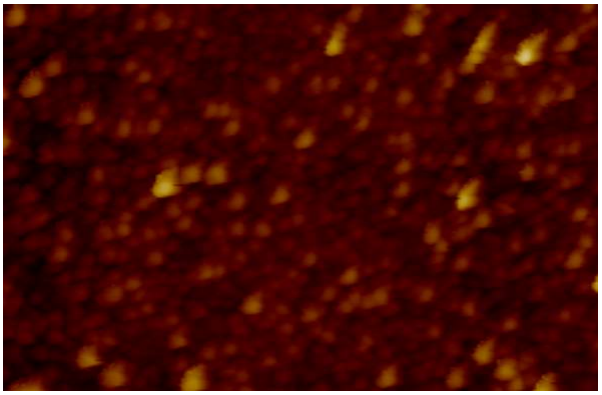


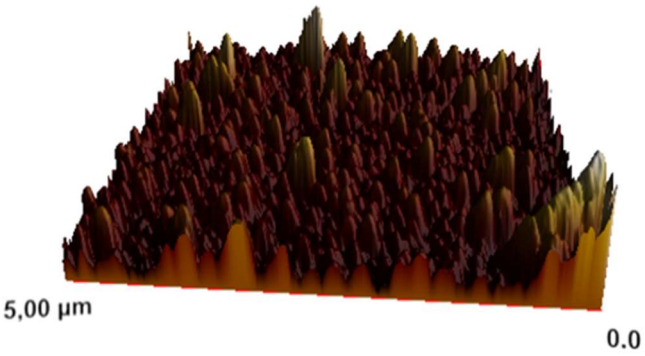
Figure 9. SEM micrographs of the ZnO films of 240 nm after annealing

As the film thicknesses increase from 80 nm to 240 nm, after annealing, these nanorods grow columnar way. As seen from Fig. 7-9, diameters of nanorods increase and completely cover the surface. Considering the XRD studies of 132-240 nm thick films, these nanostructures, which show the transition from Zinc (Zn) weighted phases to Zinc-oxide (ZnO) phases, depend on increased oxygen content.

3.3 AFM analysis of the ZnO films



(a)

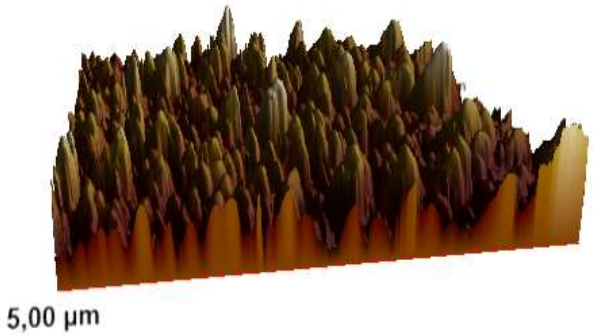


(b)

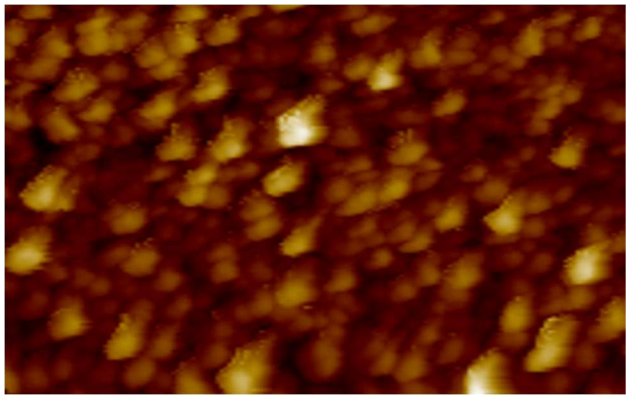
Figure 10. AFM images of the ZnO films with thicknesses of 80 nm after annealing a) 3D-AFM b) 2D-AFM

AFM images of ZnO films are shown in Fig.10-11. These figures reveal that nanorods grow in a columnar way. In addition, these nanorod structures come together along the surface to form nanorod clusters.

AFM analysis shows us mean nanorod sizes (length) increase from 297 nm to 335 nm for the film thickness of 80 nm, 240nm, respectively. As seen from Fig.10 and Fig.11, if the film thicknesses increase from 80 nm to 240 nm, after annealing, grain diameters increase, and ZnO clusters occur. At the same time, the columnar growths occur in the zinc oxide structures. Furthermore, the intensity of ZnO phases increases according to the XRD analysis. Therefore XRD, SEM and AFM analyzes are compatible with each other.



(a)



(b)

Figure 11. AFM images of the ZnO films with thicknesses of 240 nm after annealing a) 3D-AFM b) 2D-AFM

4. CONCLUSIONS

In this study, ZnO film samples with different thicknesses were obtained by thermal evaporation of high purity ZnO particles followed by annealing in the air atmosphere. The effect of film thickness on ZnO formation was investigated. XRD analysis shows that ZnO structures were not observed for all the deposited films. These films have only Zn phases. In thinner films (80-100) nm, after annealing, Zn phase intensities decrease, but in thick films (132-240) nm, Zn phases disappear and ZnO phases visible. This indicates that the Zn phases replaced by ZnO. This is an evidence that the film thickness is important as well as the annealing temperature so that zinc oxide films can be formed. Moreover, ZnO films obtained by annealing after thermal evaporation exhibit a polycrystalline structure.

SEM and AFM analysis show that all ZnO films are formed as nanorods, and they completely cover the surface. If the film thicknesses increase, after annealing, grain diameters increase and ZnO clusters occur.

Finally, we can say that from the characterization results of ZnO samples in the thickness between 132- 240 nm, which were annealed at 300 °C for two hours, have the best physical properties. These ZnO nanorod structures with good structural properties are preferred in optoelectronics and sensor applications widely.

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