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Production and Characterization of Al-Doped ZnO Thin Films with Sol-Gel Magnetic Spin Coating Technique

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Abstract

In this study, ZnO thin films were developed by using Sol-Gel Spin Coating method which is simpler than other methods and by using low cost Sol-Gel Magnetic Spin Coating method which will be used for the first time in literature. Some physical properties of ZnO thin films produced by doping 1%, 3% and 5% Al were examined using X-Ray Diffraction (XRD) Device, Field Emission Scanning Electron Microscope (FESEM) and UV-Vis Spectrophotometer. When structural properties were examined, it was seen that preferential orientation changed and crystallite size values increased as Al doping amount increased. When the surface properties were examined, it was seen that a homogeneous coating was formed on the litter with the technique used. In addition, FESEM images prove that crystallite size values increase as the amount of doping increases. It was determined that the band gap values of thin films whose optical properties were examined decreased as the amount of doping increased. As it can be understood from these results, this thin film production technique, which is used for the first time in the literature, is able to produce doped thin films more easily and economically.

Keywords: ZnO, Al doping, thin film, sol-gel, magnetic spin coating

1. INTRODUCTION

Semiconductor thin films can be obtained by many techniques such as spray pyrolysis [1], laser etching [2], magnetron spray [3], chemical bathing [4], thermal evaporation [5] and sol-gel [6]. Having high optical permeability [7] and wide bandwidth [8], ZnO thin films are widely used for experiments because they are environmentally

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sensitive, free of toxic substances [9], easily accessible, useful and cost effective. The new generation of semiconductor ZnO thin films have many uses such as gas sensors [10], organic waste water treatment [11], photovoltaic fields [12], optoelectronic devices [13], biosensors [14], flexible or wearable UV light sensors [15], biomedical applications [16] and surface acoustic wave (SAW) devices [17].

ZnO thin films can have different properties by doping with the help of metal elements such as Sn, Ga, In [18], S1 [19], Mg [20], Ag [21], Sa [22] and Al [23], [24]. In previous studies, it was found that the electrical conductivity of the metal-doped ZnO molecule increased [25] and that its optical properties changed [26]. It was also observed that the surface morphology of the molecule [27] and the adsorption energy [28] also changed.

In this study, 1%, 3%, 5% Al doped ZnO thin films were produced with the low-cost Sol-Gel Magnetic Spin Coating method which will be used for the first time in the literature by developing the Sol-Gel Spin Coating method which is simpler than the other methods, and structural, morphological and optical properties were examined.

2. EXPERIMENTAL METHOD

In this study, ISOLAB brand microscope slide was used as base material for thin films produced. Microscope slides were cut as 20mm x 20mm. The cut glass substrates were cleaned following the necessary procedure and made suitable for film coating.

The sol-gel solution, which would be used to produce Al doped ZnO thin films, was prepared as 0.75 M. For this sol-gel solution, Zn $(CH_3COO)_2.2H_2O$ (zinc acetate dihydrate), 2-methoxyethanol as the solvent and monoethanolamine (MEA) as the stabilizer were used. Al $(NO_3)_3.9H_2O$ (aluminium nitrate nonahydrate) was used for Al doping. Doping was carried out by adding 1%, 3% and 5% aluminium nitrate nonahydrate to ZnO solution. The prepared solutions were stirred at room temperature for 3 hours and allowed to stand at room temperature for 2 days.

After the solution preparation step was completed, the coating step was started by magnetic rotation on the cleaned glass bases. In order to produce thin films whose test parameters were determined, the glass mats were conveniently placed on the magnetic platform, which could rotate at high speeds. The determined amount of solution was dripped with the help of a micropipette to the centre of the glass base to distribute evenly throughout the glass base, and magnetic rotation was started at a rotation speed of 3000 rpm. When the rotation time was completed, the glass substrates were removed and heat-treated in the oven at 100°C for 10 minutes to dry. Drying is a necessary process to evaporate the solution retained on the surface and to remove the organic compounds from the surface. These processes for one coat of coating were repeated to obtain 9-ply films. The films were then annealed in air at 500°C for 2 hours. The structural and morphological characterizations of 3 series with 1%, 3% and 5% Al dopes were made by using X-ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM), and the effects of the doping were compared with the undoped ZnO series. Undoped thin films were named as ZnO, 1%, Al-doped thin films as AZO1, 3%, Al-doped thin films as AZO3, 5%, Al-doped thin films as AZO5.

3. RESULTS AND DISCUSSION

PANALYTICAL Empyrean X-Ray Diffraction (XRD) device was used to examine the structural properties of the obtained films. The operating conditions of the device were 45 kV voltage and 40 mA current. The scanning rate was selected as 2 degrees/minute, CuK_α beam with a wavelength of 1,5406 Å was used and samples were examined at the limit values of $30^o \leq 2\theta \leq 60^o$. The obtained structures were compared with ICDD (International Center for Diffraction Data): 98-003-1052 card for hexagonal ZnO. Figure 1 shows comparative XRD analysis spectra of undoped ZnO and doped AZO thin films.

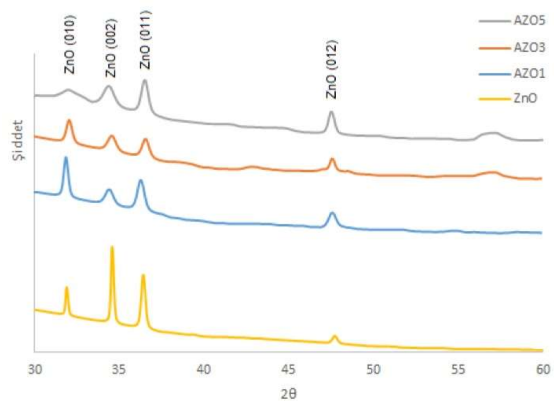

Figure 1. Comparative XRD analysis spectrum of undoped ZnO and doped AZO thin films.

As seen from the XRD spectra, all series are polycrystalline. In the undoped ZnO series films, 4 peaks of the hexagonal ZnO structure ((010), (002), (011) and (012)) are observed. There is no peak of the Al structure at 3% and 5% doping ratios with the effect of Al, which is doped as 1% since AZO1 series. On the contrary, peak intensities decreased significantly as the amount of doping increased. From these results, it is understood that the level of crystallization decreases as Al ratio dopped to ZnO structure increases. In addition, while the preferred orientation peak in the pure ZnO structure is (002), the preferred orientation began to change after Al started to be doped. In the AZO1 and AZO3 series, where 1% and 3% were doped, preferred orientation was seen as (010) peak, whereas in the AZO5 series formed with 5% Al doping, preferred orientation was observed as (011) peak. According to these results, preferential orientation of ZnO structure can be changed by Al doping.

The average crystallite size (D) values were calculated by using Scherrer Formula with the information obtained from XRD spectra.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

In the formula; λ is the wavelength of the x-ray used, θ is the diffraction angle and β is the half-peak width in radians [29]. Table 1 shows the calculated particle size values of doped AZO thin films and undoped ZnO. As can be seen from the table, the average crystallite size values increase as the amount of doping increases.

Table 1. Crystallite size values of undoped AZO thin films and doped ZnO

Seri	D (nm)
ZnO	112
AZO1	132
AZO3	155
AZO5	186

ZEISS Supra 40VP Field Emission Scanning Electron Microscope (FESEM) was used to examine the surface properties of the obtained films. Figure 2 shows FESEM images at 100kx magnification of undoped ZnO and doped AZO thin films.

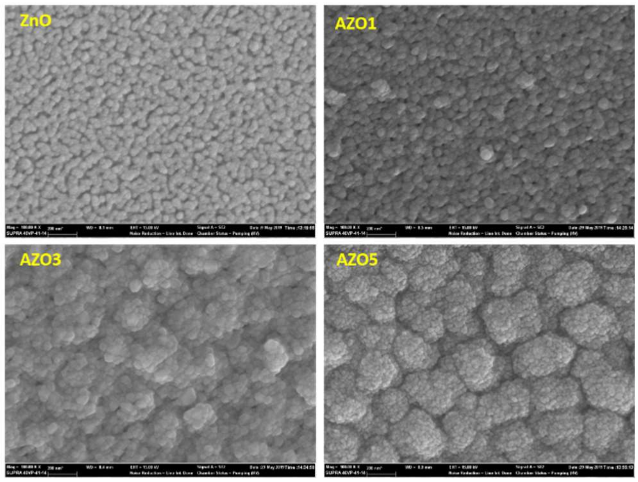

Figure 2. Comparative FESEM images of undoped ZnO and doped AZO thin films.

When FESEM images were examined, it was seen that the film was composed of particles of nanoscale which were nearly homogeneously distributed over the entire surface and there were no gaps on the surface, so that the grains were better attached to each other. In addition, it was observed that crystallite size values started to increase with doped Al and these grains increased as the amount of doping increased. These results are consistent with the results of crystallite size values obtained from XRD spectrum.

UV-Vis Spectroscopy measurements were performed on the PERKIN ELMER LAMBDA 25 device in the wavelength range of 300 - 1100 nm to examine the optical properties of the films obtained. By using the basic absorption spectrum data obtained from UV-Vis Spectroscopy measurements, the change graphs of each film $(\alpha h\upsilon)^2$ by hυ are drawn in order to determine the band gap values of the films. The energy values of the point at which the linear part of these graphs intersect the hυ axis at $(\alpha h\upsilon)^2 = 0$ are determined as the band gap values of the films. This method is known as the Tauc Method [30]. Figure 3 shows the comparative change of $(\alpha h\upsilon)^2$ by hυ. Additionally, the band gap values of thin films are given in Table 2.

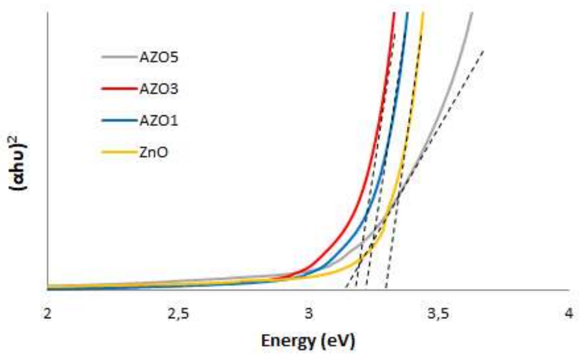

Figure 3. The change of $(\alpha h\upsilon)^2$ by hυ.

Table 2. Band gap values of thin films

Seri	Band Gap (eV)
ZnO	3.31
AZO1	3.25
AZO3	3.18
AZO5	3.10

As can be seen from the table, while the band gap values in the undoped ZnO series was 3.31 eV, this value started to decrease with Al doping. As the amount of doping increased, the value of the band gap decreased. This decrease was due to the increase in crystallite size values as the amount of doping increased. These results are consistent with the values found for Al-doped ZnO thin films in the literature.

4. CONCLUSION

In this study, ZnO thin films with undoped and Al doped were produced by using Sol-Gel Magnetic Spin Coating Technique which is a much simpler and cheaper technique than other thin film production techniques. Some physical properties of the thin films were characterized by X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and UV-Visible Spectrophotometer. By doing so, we aimed to show that our newly developed thin film coating technique can be used in the production of doped thin films. XRD analysis showed that all thin films were polycrystalline. No peak of Al structure was observed in 3% and 5% doping ratios due to the effect of Al, which was added as 1% since AZO1 series. On the other hand, peak intensities decreased significantly as the amount of dope increased. From these results, it was understood that the level of crystallization decreased as Al ratio increased to ZnO structure. In addition, it was observed that preferential orientation of ZnO structure can be changed by Al doping. Crystallite size values also increased as the amount of doping increased. When FESEM images were examined, it was seen that all films were composed of particles of nanoscale and there were no gaps on the surface, so that the particles were better attached to each other. Additionally, it was observed that crystallite size values started to increase with Al doping and these grains increased as the amount of doping increased. Band gap values obtained by UV-Vis Spectroscopy measurements decreased as the amount of doping increased. These results are consistent with the values found for Al-doped ZnO thin films in the literature. As it can be understood from this study, the thin films doped with the Sol-Gel Magnetic Spin Coating Technique, which was used for the first time in the literature, could be produced more easily and economically.

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