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ERKEN GÖRÜNÜM

Effects of heat treatment time on properties of 1% Fe-doped ZnO films fabricated by ultrasonic spray pyrolysis

Isıl işlem süresinin ultrasonik kimyasal püskürtme ile üretilen %1 Fe katkılı ZnO filmlerin özellikleri üzerine etkileri

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Effects of Heat Treatment Time on Properties of 1% Fe-Doped ZnO Films Fabricated by Ultrasonic Spray Pyrolysis

Highlights

- *Effect of heat treatment time on ZnO thin films*
- *Thin film produced by ultrasonic spray pyrolysis*

Graphical Abstract

The photocatalytic behaviors of thin films vary depending on the temperature and time of heat treatment. This study examined the changes in the properties of 1% Fe-doped ZnO thin films produced by the ultrasonic spray pyrolysis method based on the heat treatment time.

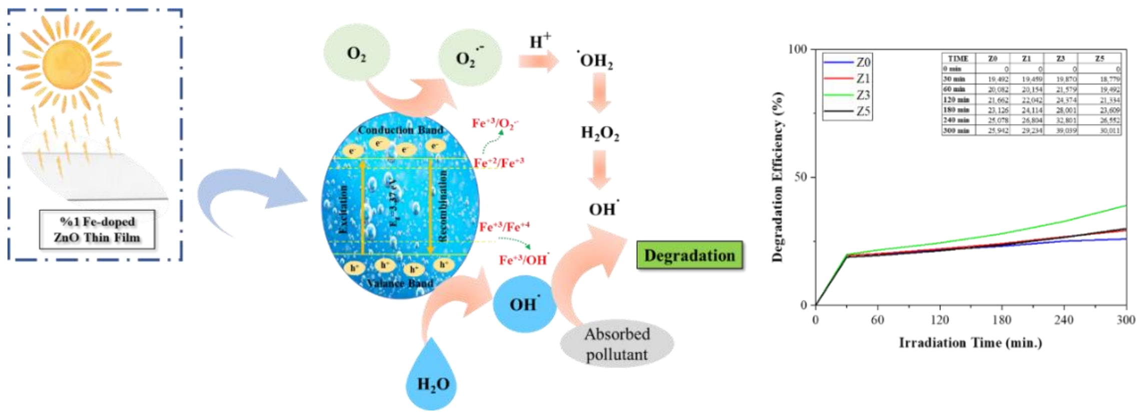

Figure. Schematic representation of photocatalysis for %1 Fe-Doped ZnO and

Aim

The study investigates the effect of different heat treatment durations on the structural, morphological, and photocatalytic properties of 1% Fe-doped thin films produced by the ultrasonic spray pyrolysis method.

Design & Methodology

1% Fe-doped ZnO (Z0) films were deposited on glass substrates using ultrasonic spray pyrolysis at a substrate temperature of 350±5 °C. After deposition, the films were subjected to heat treatment at 500 ℃ for different durations (1 hour, 3 hours, and 5 hours) under atmospheric conditions

Originality

The heat treatment time has been determined to affect the structural and optical properties of 1% Fe-doped ZnO films produced by ultrasonic spray pyrolysis.

Findings

Z3 was found to have the best photocatalytic degradation behavior compared to Z1 and Z5 samples.

Conclusion

The increase in heat treatment time has a positive effect on photocatalytic degradation until it causes an increase in crystallite size.

Declaration of Ethical Standards

This article's author(s) declares that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Effects of Heat Treatment Time on Properties of 1% Fe-Doped ZnO Films Fabricated by Ultrasonic Spray Pyrolysis

Araştırma Makalesi/ Research Article

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ABSTRACT

In this study, 1% Fe-doped ZnO thin films were deposited using Ultrasonic Spray Pyrolysis (USP) to examine their structural, morphological, and photocatalytic properties. Heat treatment was applied to 1% Fe-doped ZnO thin films produced with USP at 500 ºC for different times (1, 3, and 5 hours). The results of the samples heat-treated for different times were compared with the as-deposited sample in terms of morphological, structural properties, and photocatalytic degradation efficiency. It was observed that the ZnO thin films with a heat treatment time of 3 hours had more distinct crystal structures, and their surface morphologies were more regular and homogeneous. When the photocatalytic behaviors were examined, it was determined that the degradation efficiency of the samples heat-treated for 3 hours was better than the other samples. In conclusion, this study shows that the heat treatment time of 1% Fe-doped ZnO thin films deposited by USP significantly affects the films' structural, morphological properties, and photocatalytic activity behaviors. These results emphasize that the heat treatment time of 3 hours should be preferred and guide future research in thin film production and photocatalytic applications.

Keywords: Fe-doped ZnO, Heat treatment, Ultrasonic spray pyrolysis (USP), Structural properties, Photocatalytic activity

Isıl İşlem Süresinin Ultrasonik Kimyasal Püskürtme ile Üretilen %1 Fe Katkılı ZnO Filmlerin Özellikleri Üzerine Etkileri

ÖZ

Bu çalışmada; morfolojik, yapısal ve fotokatalitik özelliklerini incelemek amacıyla Ultrasonik Kimyasal Püskürtme yöntemi kullanılarak %1 Fe katkılı ZnO ince filmler üretilmiştir. UKP ile üretilen %1 Fe katkılı ZnO ince filmlere 500 ºC'de farklı sürelerde (1, 3 ve 5 saat) ısıl işlem uygulanmıştır. Farklı sürelerde tavlanan numunelere ait sonuçlar, ham numune ile morfolojik, yapısal özellikler ve fotokatalitik bozunma verimliliği açısından karşılaştırılmıştır. Isıl işlem süresi 3 saat olan ZnO ince filmlerinin daha belirgin kristal yapılara sahip olduğu ve yüzey morfolojilerinin daha düzenli ve homojen olduğu görülmüştür. Fotokatalitik davranışları incelendiğinde 3 saat ısıl işlem gören numunlerin bozunma verimliliğinin diğer numunelerden daha iyi olduğu belirlenmiştir. Sonuç olarak bu çalışma, ultrasonik kimyasal püskürtme yöntemiyle üretilen %1 Fe katkılı ZnO ince filmlerin tavlama süresinin filmlerin yapısal, morfolojik ve optik özelliklerini önemli ölçüde etkilediğini göstermektedir. Bu sonuçlar, özellikle 3 saatlik tavlama süresinin tercih edilmesi gerektiğini vurgulayarak ince film üretimi ve fotokatalitik uygulamalarda gelecekteki araştırmalara rehberlik etmektedir.

Anahtar Kelimeler: Fe katkılı ZnO, Isıl işlem, Ultrasonik kimyasal püskürtme (UKP), Yapısal özellikler, Fotokatalitik aktivite

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1. INTRODUCTION

Developing photocatalytic applications and semiconductor materials has recently become very important in eliminating environmental problems. Among semiconductor materials, ZnO thin films have attracted attention due to their properties such as high light sensitivity [1], chemical stability [2], high photocatalytic activity [3], low cost [4], and are seen as a promising material in photocatalysis, and self-cleaning surface applications [3, 5, 6]. Numerous studies have been conducted to regulate and improve the photocatalytic properties of ZnO thin films. These include studies based on many factors, such as element doping, heat treatment conditions [7, 8], and other production methods [9-11]. Many studies are in the literature, especially on elemental doping [6, 12-14]. In particular, studies on Fe-doped ZnO films have reported that they exhibit exciting properties such as improved electrical conductivity, optical absorption, and magnetic behavior [15-18]. In addition, the optimization of Fe-doped ZnO thin films can also be enhanced by the influence of various process parameters, including heat treatment conditions. Heat treatment profoundly affects thin films' structural, optical, and electrical properties [8, 13]. Defects and structural changes occur in heat-treated Fe-doped ZnO thin films. It also becomes possible to

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change the band gap energy. Thus, it significantly affects the performance of the material in applications. In addition, it has been stated in literature studies that morphological, structural, optical properties, and photocatalytic behavior change with the defects created, grain sizes, porosity, and roughness, depending on the production methods [5, 19-21]. However, to our knowledge, while the effect of heat treatment on the physical properties of 1% Fe-doped ZnO oxides produced by the ultrasonic spray pyrolysis method has been studied, the effect of heat treatment time has not yet been reported in the literature.[22].

In this study, 1% Fe-doped ZnO thin films were synthesized via the ultrasonic spray pyrolysis (USP) technique. The influence of heat treatment parameters, particularly duration and temperature, plays a crucial role in optimizing thin films for technological applications. To systematically investigate the effects of annealing time on the structural, morphological, and photocatalytic properties of Fe-doped ZnO thin films, heat treatment was conducted at 500°C in an open atmosphere for 1, 3, and 5 hours. Structural and optical characterizations were performed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis spectroscopy to elucidate changes in crystallinity, surface morphology, and photocatalytic activity. The findings offer valuable insights into the correlation between annealing duration and material properties, contributing to the optimization of Fe-doped ZnO thin films for advanced applications.

2. MATERIAL AND METHOD

2.1. Material

In this study, the production of ZnO thin films doped with 1% Fe by volume ratio was carried out using 0.1 M Zn[$(CH_3COO)_2$Zn.2H2O] (purity ≥99.5%, ISOLAB) and $FeCl_3$ (purity ≥98%, TEKKİM) as Zn and Fe sources, respectively. HCl was also added to facilitate dissolution.

2.2. Process

Before thin films were fabricated by ultrasonic spray pyrolysis (USP), the glass substrates were cleaned with water, detergent, ultrapure water, and ethanol, respectively. Spray solutions were prepared with ultrapure water and 0.1 M Zn[$(CH_3COO)_2Zn.2H_2O$] and $FeCl_3$. By adding $FeCl_3$ to the Zn[$(CH_3COO)_2Zn.2H_2O$] solution, the Fe ratio of the main solution was ensured to be 1% by volume. To facilitate dissolution, 3 ml HCl was added to the created solution and mixed with a magnetic stirrer at 25ºC for approximately 30 minutes. Thin film production was carried out in a USP (IDASONIC, AVE-USP-200S, Turkey) at a hot plate temperature of 350±5 °C. First, the glass substrates and the solution were positioned in the hot plate and solution chamber in the USP system. The distance between the glass substrates and the ultrasonic nozzle was set to 30 cm. While compressed dry air with a pressure of 0.7 atm was chosen as the carrier gas, the flow rate of the solution was determined as 5 cc/min. The flow rate of the precursor solution was monitored using an ultrasonic nozzle (100kHz) connected to a flow meter. The starting solution volume was set to 100 ml. The spraying time was carried out in 20 minutes.

Heat treatment was then applied to the 1% Fe-doped ZnO thin films produced. In order to examine the effect of heat treatment time on the produced films, the heat treatment was applied at different heat treatment times (1 hour, 3 hours, 5 hours), under open atmosphere conditions, and at a temperature of 500 °C. The cooling process was carried out in the oven under ambient conditions until room temperature. The samples were named Z0, Z1, Z3, and Z5 according to the heat treatment time, shown in Table 1. For example, samples without heat treatment (only as-deposited) are shown as Z0, and samples heat treated for 1 hour are shown as Z1.

2.3 Characterization

The structural characterization of both as-deposited and heat-treated 1% Fe-doped ZnO thin films was conducted using a Bruker D8 Advance Diffractometer. Structural analyses were performed using CuK$_\alpha$ radiation (λ = 1.5406 Å) within the 2θ range of 20° to 80°, with a step size of 0.02°. Peak intensities (*I*), peak positions (*2θ*), and full width at half maximum (*FWHM, β*) values were obtained from XRD data in order to calculate texture coefficients (*P*), crystallite sizes (*D*), macrostrains (*e*), and dislocation densities (□). For this purpose, the equations given below were used [23, 24].

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

$$\delta = \left(\frac{1}{D}\right)^2 \tag{2}$$

$$< e > = \frac{d - d_0}{d_0} \tag{3}$$

$$P_{(h_ik_il_i)} = \frac{I_{(h_ik_il_i)}}{I_{0(h_ik_il_i)}} = \left[\frac{1}{n}\sum_{i=1}^{n}\frac{I_{(h_ik_il_i)}}{I_{0(h_ik_il_i)}}\right]^{-1} \tag{4}$$

Here, □□denotes the Bragg angle, while *d* and d_0 represent the interplanar spacing with and without deformation, respectively. Additionally, I_0 is the standard intensity obtained from the ICDD, *I* refers to the observed intensity of the ($h_ik_il_i$) plane, and n represents the most intense three peaks.

Surface morphologies were investigated using HITACHI SU5000 FE-SEM. Photocatalytic degradation behaviors of the deposited films were analyzed using a Shimadzu brand UV/Vis 2600 model spectrophotometer with a 400-800 nm photon range. Photocatalytic degradation behaviors of films were performed using methylene blue (MB, $C_{16}H_{18}ClN_3S.3H_2O$, Carlo Erba) dye solution under a UV lamp (15W-254 nm). The absorption spectra of the MB aqueous solutions in light and dark ambients were taken in the 400–800 nm wavelength range. For photocatalytic degradation tests, films were cut to the same size (10x10 mm) and placed in beakers. Then, 10 mL of MB solution was added into beakers for each thin film. The beakers were positioned under the UV lamp so that the distance between the MB solution and the UV lamp was 150 mm. Absorbance spectra were measured first for 30 minutes and then for 60 minutes with a Shimadzu UV/Vis 2600 spectrophotometer device in the wavelength range of 400-800 nm to determine the alterations in the solution concentration.

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Table 1. Display and explanation of sample codes

Production Parameters	**Sample Codes**
%1 Fe doped, as-deposited	Z0
%1 Fe doped, 500 °C - 1 hour heat treated	Z1
%1 Fe doped, 500 °C - 3 hour heat treated	Z3
%1 Fe doped, 500 °C - 5 hour heat treated	Z5

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

The crystal structures of as-deposited and different times heat-treated %1 Fe-doped ZnO thin films were characterized by X-ray diffraction (XRD), which is given in Figure 1. The XRD data were evaluated with reference to ICDD 00-036-1451. The detailed properties of each film were analyzed based on peak positions (2θ), peak intensities (I), and FWHM (β). When the XRD patterns were compared with the reference pdf card, it was determined that each pattern had sharp and intense diffraction peaks corresponding to the (100), (002), (101), (102), (110), (103) and (112) planes related to the hexagonal wurtzite crystal structure of ZnO. When each thin film pattern was examined, no secondary phase peaks belonging to the element or compounds of the dopant iron (Fe) were observed. This result shows that the dopant element was well integrated into the lattice regions during the ultrasonic spraying process. As seen in Figure 1, the intensity of the (002) peak and the full-width half maximum (FWHM) change depending on the heat treatment times. It is seen that the most intense peaks in the XRD patterns of all samples belong to the (002) plane. Also, Table 2 shows that all samples have a preferred orientation to the (002) plane.

A sample with randomly oriented crystallite yields gives $P_{(hkl)} < 1$; the larger this value, the greater the amount of crystallites oriented at the (hkl) direction [25]. If the P value is 1 and greater than 1, it shows a preferential orientation. According to the calculations, it was determined that all samples except the Z0 sample had preferential orientation only to the (002) plane. It has been determined that the Z0 sample has a dominant growth orientation to the (100) plane and the (002) plane. ZnO thin films generally have a wurtzite crystal structure, and the (002) plane with the lowest surface energy is preferred during growth. The increment in the (002) plane with the effect of heat treatment could be attributed to the improved crystal structure, stress relief, and reduction of oxygen vacancies.

The intensity of the (002) peak and the FWHM value depend on heat treatment. The fact that the (002) peak has the highest intensity indicates that the growth is along the c-axis [26]. The peak intensities of the (002) plane of the heat-treated samples are much higher than the as-deposited sample. On the other hand, it was observed that the peaks shifted after the heat treatment process. The 2θ value as-deposited film related to (002) plane, which was determined at 34.162°, changed to 34.30°, 34.418°, and 34.497° values for heat-treated films. However, it was observed that the 2θ value shifted towards higher angles depending on the heat treatment time. The reason for the 2θ value shifting towards the high angle can be described as the release of internal stresses by the effect of heat treatment. It can be said that heat treatment time and temperature have similar effects on the structural and morphological properties of ZnO films [27].

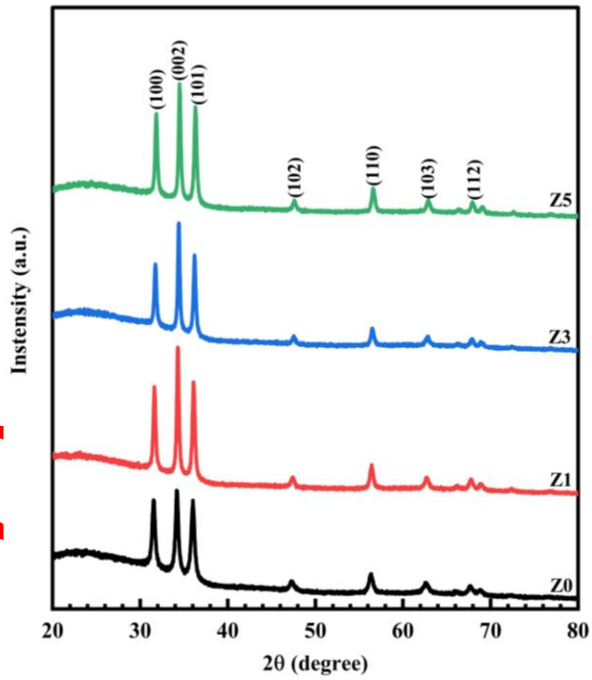

Figure 1. XRD pattern of as-deposited and heat-treated %1 Fe-doped ZnO thin films at different times

Another indicator that internal stress decreases with heat treatment is the decrease in the distance between planes. The interplane distance (d) for samples Z0, Z1, Z3, and Z5 was calculated as 2.6299, 2.61229, 2.60358, and 2.59781, respectively, and is shown in Table 2. It was determined that the distance between planes decreased with increasing heat treatment time. The reason for this decrease can be associated with the reduction of internal stresses due to heat treatment.

Mathematical calculations were performed using the appropriate formula given in the literature in order to determine FWHM (β), crystallite sizes (D), macrostrain (e), and dislocation densities (δ) for the three major peaks shown in Table 3 [27, 28]. Macrostrain calculations were made using equation 3, and values have changed from 0,01021 to -0,00212. In thin films, the negative sign indicates the tensile stress state. Therefore, it can be said that the strain type changed in the sample subjected to the heat treatment process for 5 hours. In other words, it can be said that after 5 hours of heat treatment, the compressive stress gave way to the tensile stress.

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Table 2. Structural parameters to three major peaks from XRD patterns and ICDD values

Sample	Miller Indice (hkl)	2θ	$2\theta_0$	I	I_0	d	d_0	P
Z0	**(100)**	31.578	31.77	4840	57	2.843	2.814	**1.011**
	(002)	34.162	34.422	5321	45	2.629	2.603	**1.408**
	(101)	36.016	36.253	4872	100	2.502	2.476	0.580
Z1	**(100)**	31.617	31.77	5208	57	2.827	2.814	0.911
	(002)	34.3001	34.422	6981	45	2.612	2.603	**1.547**
	(101)	36.095	36.253	5427	100	2.486	2.476	0.541
Z3	**(100)**	31.736	31.77	4297	57	2.817	2.814	0.874
	(002)	34.418	34.422	6140	45	2.603	2.603	**1.582**
	(101)	36.213	36.253	4698	100	2.478	2.476	0.545
Z5	**(100)**	31.854	31.77	5010	57	2.807	2.814	0.934
	(002)	34.497	34.422	6354	45	2.598	2.603	**1.501**
	(101)	36.292	36.253	5320	100	2.473	2.476	0.565

Table 3. Calculated structural parameters of %1 Fe-doped ZnO thin films

Sample	Miller Indice (hkl)	β (FWHM)	D(nm)	$\langle \varepsilon \rangle$	δ (line/nm^2)
Z0	**(100)**	0.394	23.293	0.01023	0.00184
	(002)	0.368	25.105	0.01021	0.00159
	(101)	0.409	22.704	0.01064	0.00194
Z1	**(100)**	0.304	29.040	0.00470	0.00119
	(002)	0.275	33.607	0.00345	0.00088
	(101)	0.332	27.976	0.00423	0.00128
Z3	**(100)**	0.299	30.705	0.00105	0.00106
	(002)	0.26	35.557	0.00066	0.00079
	(101)	0.3	30.970	0.00106	0.00104
Z5	**(100)**	0.307	29.914	-0.0026	0.00112
	(002)	0.279	33.143	-0.0021	0.00091
	(101)	0.313	29.691	-0.0011	0.00113

It is seen in Table 3 that the calculated crystallite size (D) values of films vary between 22-35 nm. The increase in the crystallite size of thin films with heat treatment indicates that grain boundaries are reduced [25]. The average crystallite size of the without heat-treated thin film was calculated as 23.7 nm. After 1, 3, and 5 hours of heat treatment, the average crystallite size was determined as 30.2, 32.41, and 30.91 nm, respectively. In addition, the dislocation density (□) values, which indicate the dislocation line length per unit volume, were determined as the minimum for the Z3 (0.000791) film. The fact that the 1% Fe doped ZnO thin film, which was heat treated for 3 hours at 500ºC in an open atmosphere (Z3), has the lowest dislocation density can be explained by the decrease in crystal structure defects in the structure and the increase in film quality due to the effect of heat treatment. On the other hand, it is observed that the macrostrain values of thin films decrease with increasing heat treatment time. In the 5-hour heat-treated thin film, the macrostrain values were obtained as negative, indicating that the decreased compressive stresses and the type of strain changed. According to the obtained data, heat-treated thin films have more advanced properties than as-deposited thin films.

3.2. Surface Characterization

Morphological examinations were carried out with FE-SEM at 30X, 2kX, and 50kX magnifications. Figure 2 shows FE-SEM images at different magnifications of only deposited and heat-treated thin films. Morphological investigations are of great importance in determining the structure of thin films. When FE-SEM images are examined, it is seen that there are changes in the morphology of thin films depending on the heat treatment time.

The as-deposited sample and the sample subjected to heat treatment for 1 hour have almost a similar surface morphology and homogeneity. However, it was determined that there were significant changes in the surface, such as growth and reduction of particle boundaries with a 3-hour heat treatment. In addition, changes in particle sizes and distribution were observed. This indicated that the surface of the film became rougher. As a result, in heat treatment times longer than 1 hour, the surface structure and morphology of the ZnO film change significantly, and an increase in particle sizes may also be observed. These changes also increase the porosity on the film surface.

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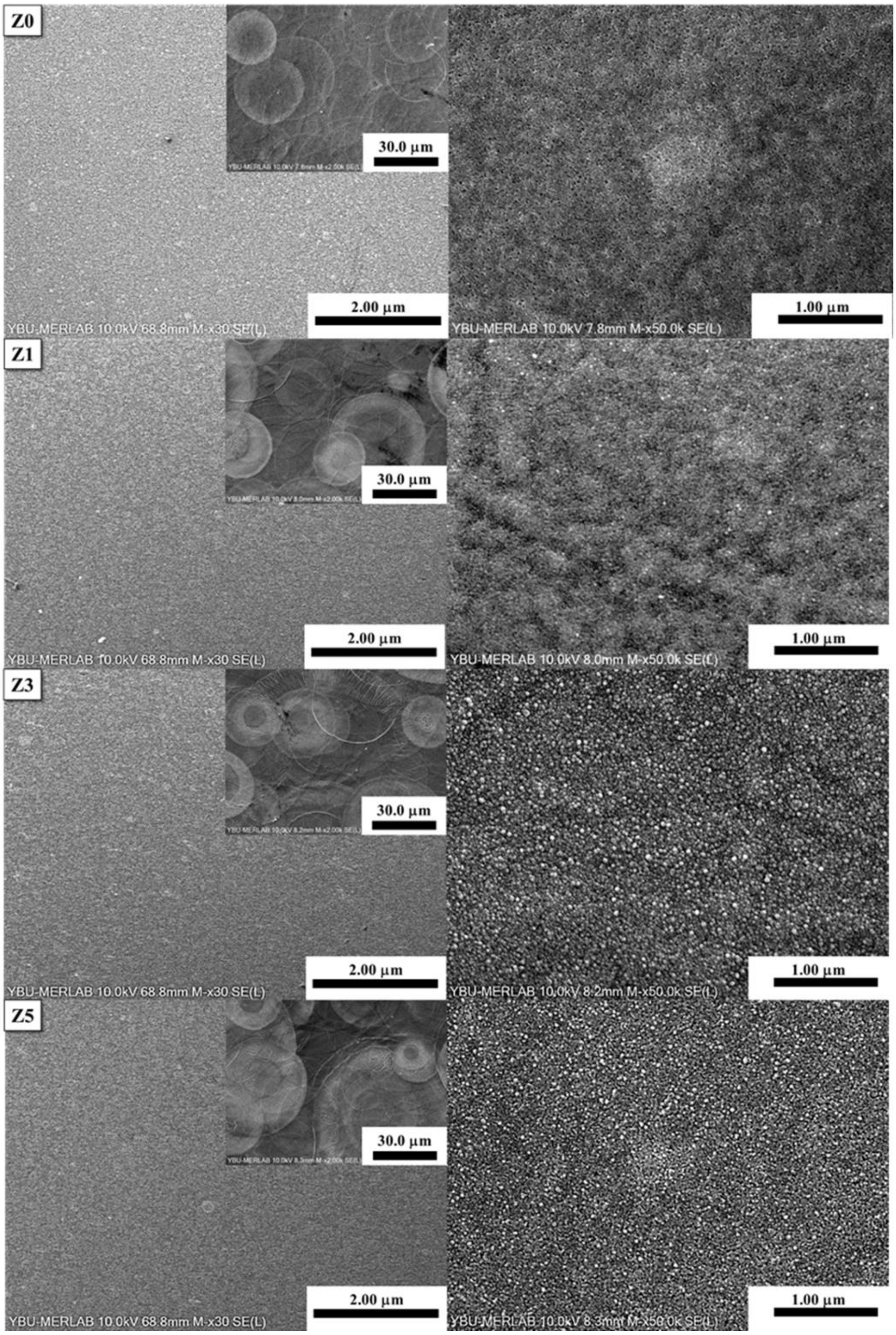

Figure 2. SEM images of as-deposited and heat-treated thin films

It is known that photocatalytic activity is related to the surface properties of thin films. In other words, surface morphology, homogeneity, roughness, and porous structure play an effective role in regulating the interaction between organic pollutants and the photocatalyst surface [27]. In particular, organic pollutants degrade faster in thin films with increased surface roughness and porosity due to the increase in specific surface area. On the other hand, it was determined that there was no linear relationship between increasing heat treatment time and morphology. When FE-SEM images of 3 hours and 5 hours heat-treated samples were compared, it was concluded that the 5 hours heat-treated sample had decreased particle size, which may be related to increased roughness and so specific surface area. This confirms the increase in crystallite sizes of Z3 film determined by the calculations performed using XRD data.

3.3. Photocatalytic Activation Analysis

At the center of photocatalytic reactions lies the exposure of a photocatalyst, suspended in a liquid solution containing organic contaminants, to UV–Vis light, inducing spontaneous adsorption. Possible reaction mechanism related to Fe-doped ZnO thin film catalyst as given below [29, 30]:

$$ZnO \xrightarrow{h\nu \geq E_g} h^+ + e^- \quad (5)$$

$$H_2O + h^+ \rightarrow OH^{\cdot} + H^+ \quad (6)$$

$$h^+ + OH^- \rightarrow OH^{\cdot} \quad (7)$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \quad (8)$$

$$O_2^{\cdot -} + H^+ \rightarrow HO_2^{\cdot} \quad (9)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (10)$$

$$H_2O_2 + O_2^{\cdot -} \rightarrow OH^{\cdot} + OH^- + O_2 \quad (11)$$

$$OH^{\cdot} + dye \rightarrow dye\ mineralization \quad (12)$$

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \quad (13)$$

$$Fe^{2+} + h^+ \rightarrow Fe^{3+} \quad (14)$$

$$Fe^{3+} + h_{vb}^+ \rightarrow Fe^{4+} \quad (15)$$

$$Fe^{4+} + OH^- \rightarrow Fe^{3+} + .OH \quad (16)$$

$$Fe^{3+} + e_{cb}^- \rightarrow Fe^{2+} \quad (17)$$

$$Fe^{4+} + e^- \rightarrow Fe^{3+} \quad (18)$$

Figure 3 shows the absorption spectra of the MB solution and the solution-film mixtures containing MB+thin film catalysts. The curve shown as MB_dark in the graph represents the absorbance value obtained after the MB solution was left in the dark for 30 minutes without the thin film catalyst, while the absorption spectrum shown as 0th minute (MB_light) represents the spectrum obtained after the solution was excited under light. In this study, to investigate the photocatalytic activity of Z0, Z1, Z3, and Z5, thin films were placed in glass beakers containing the solution after the MB dye solution (0.1 ml MB, 6 x 10^{-6} M) was illuminated. The measurements taken from the MB solution into which the thin films were placed were first carried out in 30-minute and then 60-minute periods. Absorbance spectra are presented in Figure 3 in the wavelength range of 400-800 nm and at different time intervals (30 min., 60 min., 120 min., 180 min., 240 min., and 300 min.) in the specified periods. This figure shows the decrease in absorbance spectra with increasing duration of UV light irradiation. A change was observed in the absorbance spectrum of each sample. It was determined that most MB degradation occurred in the Z3 sample. The better MB degradation in the Z3 sample is related to its crystal structure and surface properties. Kuru and Narsat have determined related results given in their research, which subject is heat treatment temperature and Mg doping effect on structural and photocatalytic activity of ZnO thin film. They identified that the increase in surface roughness leads to an enhancement in photocatalytic activity due to the increase in the active surface area. Thus, more active catalytic surfaces are formed in photocatalytic reactions, and redox reactions are accelerated [27]. As a result, crystal behavior, particle sizes, and distributions in the Z3 sample contribute to the increase in photocatalytic activity. The degradation of the methylene blue organic dyes under UV light has been calculated by the following equation [31]:

$$Degradation\ (\%) = [(C_0 - C)/C_0]x100 \quad (19)$$

where C_0 is the starting concentration of the methylene blue solution, and C is the final concentration after degradation. It was observed from Figure 4 that the degradation efficiency varied considerably between heat-treated and as-deposited samples. Accordingly, the heat treatment process positively affects the photocatalytic activity behavior. Additionally, the degradation efficiency of the Z3 sample was determined to be approximately 39% after 5 hours of irradiation. A comparative analysis of all samples revealed that the degradation followed the order of Z3, Z5, Z1, and Z0, respectively. On the other hand, it has been observed that heat treatment time positively affects the activity for a while. The lower degradation efficiency of the Z5 sample compared to the Z3 sample can be associated with the smaller particles. Increasing grain boundaries slows down photocatalytic reactions. The fact that the deposited sample (Z0) exhibits the lowest degradation efficiency is due to the same reason as the Z5 sample. In other words, the sample with the smallest grain size has the lowest MB solution degradation efficiency. It has been clearly seen that particle sizes affect photocatalytic activity. Table 4 provides a comparative overview of the photocatalytic efficiency of various thin film photocatalysts, including ZnO and Fe-doped ZnO, benchmarked against existing literature. The observed variations in degradation efficiencies can be attributed to multiple factors, including the choice of organic dye, light source, and intensity, synthesis technique, as well as the physicochemical and structural characteristics of the films [32-35]. However, further investigations are required to comprehensively elucidate the impact of thermal treatment on the photocatalytic behavior of Fe-doped ZnO films.

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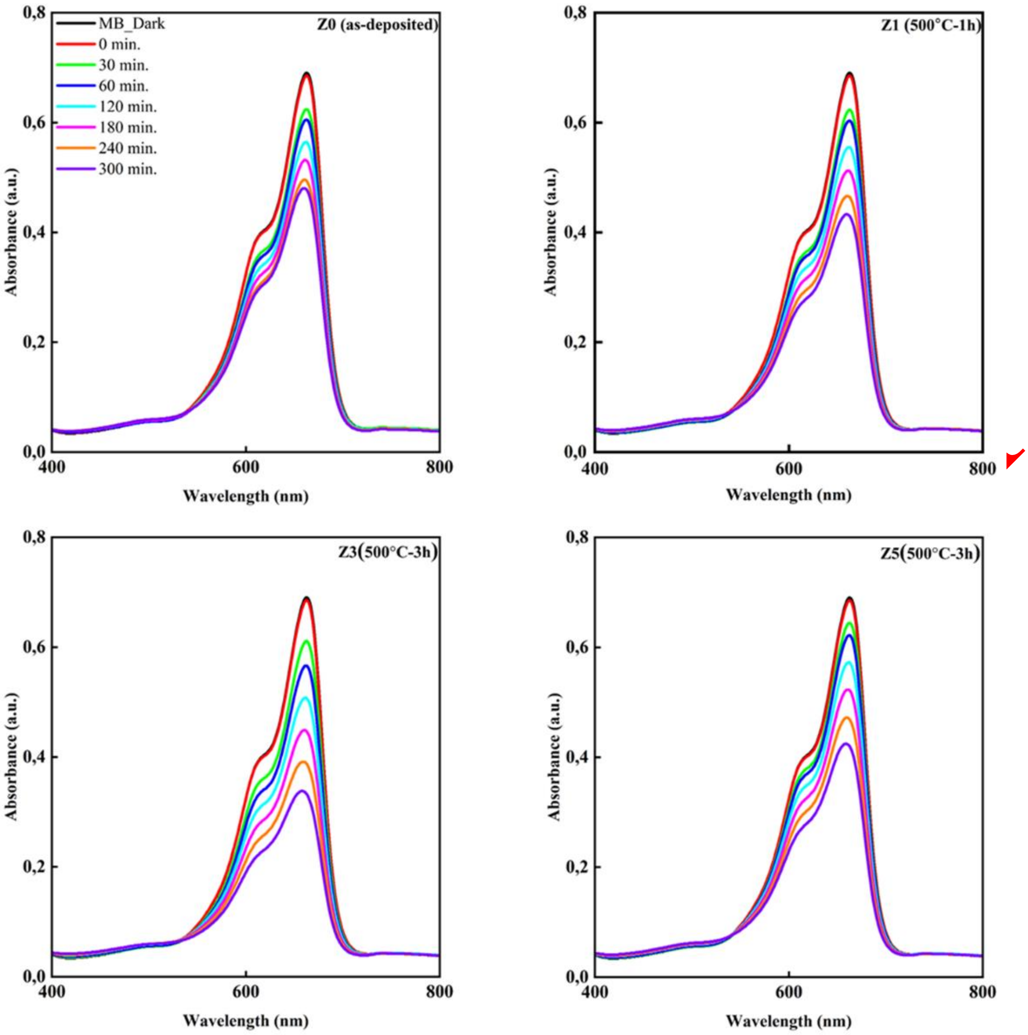
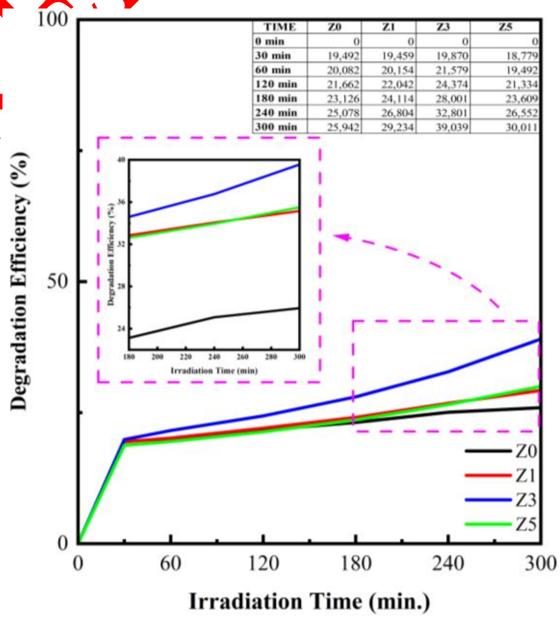


Figure 3. Photocatalytic activity of thin films at different heat treatment times



TIME	Z0	Z1	Z3	Z5
0 min	0	0	0	0
30 min	19,492	19,459	19,870	18,779
60 min	20,082	20,154	21,579	19,492
120 min	21,662	22,042	24,374	21,334
180 min	23,126	24,114	28,001	23,609
240 min	25,078	26,804	32,801	26,552
300 min	25,942	29,234	39,039	30,011

Figure 4. Effect of different heat treatment times on MB solution degradation efficiency

Table 4. Literature research of ZnO based films produced with different techniques.

Organic Dye	Sample	MB Concentration	Irridation Time	Source of Light	% Degradation Efficiency (max.)	Synthesis Technique	Reference
Methylene Blue	Fe:ZnO array films	5 mg/L	240 min.	Sunlight	95	Sol-gel	[32]
Methylene Blue	Fe:ZnO films	3 mg/L	420 min.	UV light	81	Hydrothermal method	[33]
Methylene Blue	ZnO film	30 mg/L	180 min	Visible light	85	Sol-gel dip coating	[34]
Methylene Blue	e:ZnO film	Not given	180 min.	Visible light	65	Sol-gel	[35]
Methylene Blue	Fe:ZnO films (500 °C)	6 mg/L	300 min.	UV light	39	Spray pyrolysis	Current Work

4. CONCLUSION

1% Fe-doped ZnO thin films were deposited using the ultrasonic spray pyrolysis (USP) method. After production, the films were heat-treated under an open atmosphere at 500ºC for different times (1, 3, and 5 hours). The effect of heat treatment time on thin films was discussed. No secondary phase was observed in the XRD analyses. The films changed from preferential growth direction to dominant growth direction upon heat treatment. Macrostrain decreased due to increasing heat treatment times. Then, the strain type changed from tensile strain to compressive strain. Crystallite sizes increased up to 3 hours of heat treatment. This increase may reduce the grain boundaries and increase the specific surface area. After 5 hours of heat treatment, the particles agglomerated, and the specific surface area decreased. In the microstructural analysis, changes on the thin film surface due to the effect of heat treatment were determined. Particle growth in sample Z3 was proven. The photocatalytic activity behavior of the films was examined in methylene blue (MB) solution under UV-C light. It was observed that the degradation was better in the Z3 sample. It was determined that the degradation efficiency of the heat-treated samples was much better than the Z0 sample. As a result, this study shows that 1% Fe-doped thin films heat-treated for 3 hours produced by the ultrasonic spray pyrolysis method are a potential candidate for photocatalytic applications, and alternative candidates can be created by trying various heat treatment conditions.

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DECLARATION OF ETHICAL STANDARDS

The authors of this paper declare that the materials and methods used in their study do not require ethical committee approval and/or any special legal permission.

AUTHORS' CONTRIBUTIONS

Damla Dilara ÇAKIL: Investigation, Writing, review & editing, Visualization, Formal analysis.

Meryem POLAT GÖNÜLLÜ: Conceptualization, Methodology, Investigation, Writing, review & editing.

Cemil ÇETİNKAYA: Formal analysis, Review & editing.

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CONFLICT OF INTEREST

There is no conflict of interest in this study.

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