Effect of Thickness on Photocatalytic Properties of ZnO thin films Deposited by RF Magnetron Sputtering

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Abstract - Zinc oxide (ZnO) thin films were deposited on soda lime glass substrates by using the RF magnetron sputtering technique. The deposition process was carried out in a system initially evacuated at 7x10⁻⁵ torr and a working pressure of 10⁻¹ torr in a pure argon atmosphere, at room temperature. A 2" diameter and ⅔" thick ZnO target (99.999%) was used. A target-substrate distance of 10 cm, and a working power of 125 W were kept constant. The films were deposited at different thicknesses, 50 to 400 nm. The thickness, the optical, structural and morphological properties were analyzed by profilometry, UV-Vis spectrophotometry, x-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. Additionally, three ZnO thin films were used to analyze the photocatalytic performance by using an 1x10⁻⁵ molar aqueous methylene blue (MB) solution, under the irradiation of ultraviolet light with a wavelength of 232 nm, during 5 h. The degradation of MB was carried out by absorbance measurements in the range of 400 to 800 nm every 30 min.

The ZnO films showed a wurtzite hexagonal structure with a preferential growth in the (002) planes and good homogeneity. The results obtained from the study of the degradation of methylene blue showed that the ZnO film with a thickness of 400 nm presented the best photocatalytic response.

Keywords – Zinc Oxide; Sputtering; Photocatalysis; Methylene Blue.

I. INTRODUCTION

The study of the processes used for the treatment of contaminated water has become in an interesting research area, the advanced oxidation processes (AOPs) are an example of this. Among the AOPs is found the heterogeneous photocatalysis, and coupled with this, the use of semiconducting materials as photocatalysts, which present several advantages, such as a better use of solar radiation, low cost, and the possibility of recovering the photocatalyst by certain processes when they are in powder form, or without any process in the case of thin films. Several semiconductors have been used for this purpose; however, the most studied photocatalyst is TiO₂ due to its excellent physicochemical properties, showing the highest efficiency in anatase phase, however, some other photocatalysts are being intensively used to clean contaminants in water, such as zinc oxide (ZnO) [1].

In recent years, ZnO has become in an excellent candidate in the photocatalysis area, being the main competitor of TiO₂, since they have a similar bandgap (TiO₂ - 3.2 eV), with the main advantages of being more economical and not toxic, which makes it more suitable for large-scale water treatment. ZnO has been widely used in powder form as photocatalyst, showing excellent photocatalytic efficiencies [2-4]. On the other hand, in many cases, the use of powders represents a risk to the environment, since the recovery of them after the degradation process requires certain complicated processes in some cases. In this respect, semiconducting thin films for its application in photocatalysis are intensively studied, such reports show very good results, highlighting the easy recovery of the material after the degradation.

On the other hand, the properties of the materials depend on the deposition technique. ZnO thin films have been deposited by various techniques such as sol-gel, pyrolysis spray, PLD (Pulsed Laser Deposition), CVD (Chemical Vapor Deposition), MOCVD (Metal-organic CVD), MBE (Molecular Beam Epitaxy), Sputtering, among others [5,7-9]. For photocatalytic applications of ZnO films, according to the scientific reports, these are mostly reported by chemical techniques. This fact encourages our interest in using a physical technique, namely, sputtering. In addition, it is worth mentioning that, only few works based on intrinsic ZnO as photocatalyst for degradation of methylene blue, by irradiation of ultraviolet light, are reported. In this work we report the study of sputtered ZnO thin films with different thicknesses. Additionally, the photocatalytic activity of these films is analyzed by the degradation of a aqueous solution of methylene blue in order to analyze the influence of the thickness.

II. EXPERIMENTAL

ZnO thin films deposition

ZnO thin films were deposited by RF sputtering by using a V1-System from INTERCOVAMEX. The chamber was
initially evacuated to \( \sim 7.0 \times 10^{-5} \) torr, and the working pressure was of \( \sim 5.0 \times 10^{-3} \) torr, employing an argon gas flow with a purity of 99.999 \%. A ZnO target with dimensions of 2” diameter x 1/4” thickness from Kurt J. Lesker Company (99.999\%) was used. The substrate-shutter and the substrate-thickness gauge distances were of 10 and 2 cm, respectively. The rotation speed of the substrate was maintained at 30 rpm, in order to obtain a good homogeneity of the deposited films. The substrates used were glass slides of 75 mm x 25 mm with a thickness oscillating between 0.8-1.1 mm. Initially the substrates were washed by a MOS cleaning process, for removing grease, organic materials and superficial metals. A working power of 125 W and an argon flow of 10 sccm were kept constant in all the depositions. The only variable studied was the films thickness.

Characterization of thin ZnO films

The films were characterized by different techniques, profilometry, UV-Vis spectrophotometry, x-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The films thickness was measured by profilometry by using a KLA-Tencor profilometer, model P-15, nevertheless an estimation of the thicknesses was made by using a quartz crystal contained in the deposition system. For profilometry measurement, the ZnO thin films were previously chemically etched with a water diluted hydrochloric acid solution at 20 \%. The optical properties were analyzed by UV-Vis spectrophotometry at room temperature in the range of 300-1000 nm, using a UV-2401PC spectrophotometer from Shimadzu Corporation. The thicknesses and optical constants were calculated using the Manifacier’s method. The bandgap values (Eg) were estimated by the Tauc’s method. The structural properties were analyzed by X-ray diffraction at room temperature with a PANalytical X'Pert diffractometer with the CuK\( \alpha \) radiation wavelength (1.540598 \( \AA \)) and using grazing angle (0.0333 ° / s) in the range of 20-80 ° (2-Theta). The morphological properties were studied by AFM and SEM. The profilometry equipment was also used to obtain the films roughness. An AFM analysis was developed in an area of 0.8 \( \mu \)m\(^2\), using the JSPM-5200 equipment in tapping mode. The roughness parameters (RMS-Root Mean Square) were obtained from the Gwyddion software. The SEM images were obtained from a HRSEM-AURIGA microscope, and the grain sizes were estimated from the ImageJ software.

Photocatalytic process

The photocatalytic experiment was carried out at room temperature in a cylindrical home-made reactor. The irradiation light was produced by a 15 W lamp with a wavelength of 232 nm. 0.8 cm x 1.5 cm samples were introduced in high precision quartz cells from Hellma Analytics (Art. No. 100-10-40) containing 3 ml of an 1x10\(^{-5}\) M aqueous methylene blue solution. The cells were positioned 3 cm away from the lamp. The total irradiation time was 5 h, with measurements of the optical absorbance of the testing solution every 30 min developed in a UV-2401PC spectrophotometer from Shimadzu. Three ZnO films with different thickness were selected for its photocatalytic analysis, that consists in observing the decreasing of the maximum absorption peak, located in the absorption spectra approximately at 600 nm.

III. RESULTS

Table 1 shows the deposition times and thicknesses obtained from the quartz crystal contained in the sputtering system. The average deposition rate was of the order of 3 nm/min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time (min)</th>
<th>Thickness measured from sputtering system (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-50</td>
<td>18</td>
<td>50</td>
</tr>
<tr>
<td>ZnO-100</td>
<td>38</td>
<td>100</td>
</tr>
<tr>
<td>ZnO-150</td>
<td>42</td>
<td>150</td>
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<td>ZnO-200</td>
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<tr>
<td>ZnO-300</td>
<td>83</td>
<td>300</td>
</tr>
<tr>
<td>ZnO-400</td>
<td>113</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 1. Deposition times and thickness values obtained from the sputtering system.

The film thicknesses were estimated by both, profilometry and Manifacier’s method [10] (equations 1-3), presenting an average error rate of 17 %, taking as reference the thickness obtained from the sputtering system.

Explicit formula for calculating thickness using the Manifacier’s method:

\[
    t = \frac{M\lambda_1\lambda_2}{2(n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1)} \tag{1}
\]

Where M is the number of oscillations between the two extremes (M = 1, between two consecutive maxima or minima) and \( n(\lambda_1) \) and \( n(\lambda_2) \) are the refractive index corresponding to each wavelength, which is obtained by:

\[
    n = \left[ N + \left( N^2 - n_0^2 n_1^2 \right)^{1/2} \right]^{1/2} \tag{2}
\]

\[
    N = \frac{n_0^2 + n_1^2}{2} + 2n_0n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}} \tag{3}
\]
Where $n_0$ and $n_1$ are the refractive index of the air ($n_0 = 1$) and the substrate, respectively. $T_{\text{max}}$ and $T_{\text{min}}$ are the transmittance values over the envelope functions of the interference fringes in the transmittance spectrum for the same wavelength.

Optical properties

Fig. 1 shows the transmittance spectra of the deposited ZnO films. In this figure it is possible to observe the interference fringes in the spectra, which are associated with the good crystalline quality. The absorption edge of the samples is around 380 nm, decreasing as the thickness decreases. In addition, it is observed that in films with thickness less than 300 nm the full absorption of light is not reached, as it could be expected. This fact can be explained by observing the Lambert-Bouguer’s equation (eq. 4).

$$T = e^{-\alpha t}$$  \hspace{1cm} (4)

Where $\alpha$ is the absorption coefficient and $t$ the film thickness.

The aforementioned can be exemplified as follows; if the ZnO absorption coefficient is around $160,000$ $\text{cm}^{-1}$ (≈344 nm) [11,12], and the pertinent calculations are made by means of the transmittance equation for 100 nm, we estimate a transmittance value around 20%, that matches well with the experimental result, see Fig. 1. To achieve a transmittance around 0% in the wavelength of the absorption edge, it is necessary to have a thickness equal to or greater than 300 nm.

$$D = \frac{c \lambda}{\beta \cos \theta}$$  \hspace{1cm} (5)

Where $D$ is the crystal size in nanometers, $c$ is a constant related to the shape of the profile and is very close to the unit (commonly using 0.89 or 0.9), $\lambda$ is the wavelength of radiation (usually CuKα with $\lambda \approx 1.5406$ Å) used in nanometers, $\beta$ is the FWHM used in radians, and $\theta$ is the Bragg’s diffraction angle of (in degrees).

Structural properties

Fig. 2 shows the x-ray diffraction patterns of the deposited ZnO films. The crystalline structure of all the films was identified by the reference cart ICDD (International Center for Diffraction Data) PDF no. 00-036-1451, exhibiting a wurtzite hexagonal structure. A preferential growth is observed along the (002) planes, that is, a growth along the C axis. Usually this direction is found in intrinsic ZnO films, irrespective of the growth method used, except for the epitaxial growth [13,14]. The crystal size was estimated by the Scherrer’s equation (eq. 5) by using the full width at half maximum, FWHM, of the (002) peak, obtaining crystal sizes of 10.2, 6.8, 15.7, 15.1, 6.8, 13, and 12 nm for the films ZnO-50, ZnO-100, ZnO-150, ZnO-200, ZnO-250, ZnO-300 and ZnO-400, respectively.

Morphological properties

Since the selected films for photocatalytic analysis were ZnO-50, ZnO-200 and ZnO-400, SEM characterization was performed only in these films. Fig. 3 shows SEM images of the aforementioned films, where uniform surfaces are exhibited. The 3a and 3c images present similar morphologies, showing
spherical grains shape, and an increase in grain size with the thickness from 17 to 60 nm, for ZnO-50 and ZnO-400 samples.

Whereas in the image 3b, corresponding to ZnO-200, grains with oval shapes (57 x 29 nm) are observed.

![Image of SEM images](image_url)

**Fig. 3.** SEM images. a)ZnO-50, b) ZnO-200 y c) ZnO-400.

Fig. 4 shows the bi-three dimensional images of the samples ZnO-50, ZnO-200 and ZnO-400, obtained by AFM. In the bi-dimensional images 4a, 4b and 4c it is observed that the grain size increases with the increase of the thickness of the film, coinciding with the results described by SEM. Moreover, for three-dimensional images 4a, 4b and 4c it is possible to observe pyramidal structures. The roughness values were obtained by the Gwyddion software, with values of 2.19, 7.55 and 4.16 nm for ZnO-50, ZnO-200 and ZnO-400, respectively. The roughness obtained from the samples ZnO-50 and ZnO-400 coincide well with those obtained in some other works, while the ZnO-200 film exhibits a higher value than those reported, 1 - 5 nm [15-17].

![Image of 2D and 3D AFM images](image_url)

**Fig. 4.** 2D y 3D AFM images. a)ZnO-50, b)ZnO-200 c) ZnO-400.

**Photocatalytic Activity**

The analysis of the photocatalytic activity of ZnO films was studied by monitoring the decreasing of the maximum absorption peak, corresponding to MB. In general, the photocatalytic degradation rate of several dyes is adjusted to a pseudo first-order kinetic model [18,19]. The reaction kinetics is usually expressed as eq. 6:

\[
\frac{dC}{dt} = kC^n
\]  

(6)

Where:

- \(C\) - concentration of the solution
- \(k\) - reaction rate constant
- \(n\) - order of the reaction

Since photocatalytic oxidation is governed by a first-order reaction, the eq. 7 is obtained.

\[
\frac{dC}{dt} = kC
\]  

(7)
Integrating the eq. 7, and the following initial conditions, \( t = 0, C = C_0, C' = \ln C_0 \), we obtain the eq. 9 for the reaction rate constant, \( k \), which allows to analyze the efficiency of the dye degradation.

\[
- \ln C = kt + C' 
\]

\[
- \ln \left( \frac{C}{C_0} \right) = kt 
\]  

By analyzing the degradation behavior, it can be observed that the increase of the films thickness leads to an increase in the photocatalytic activity, obtaining a significant increase for the ZnO-400 film. This sample presents a morphology with spherical shapes, the largest grain size (60 nm) and an intermediate roughness between the other two samples (4.16 nm). Several investigations comment about the possible factors influencing the photocatalytic activity, such as grain size and roughness. In this respect, it is expected that, a low grain size and a high roughness lead to high surface area, that would result in a higher photocatalytic efficiency. However, analyzing our values of grain size and roughness of the ZnO films deposited in this work, it is verified that this trend did not occur, therefore, the increase in photocatalytic activity is attributed to the increase in thickness and not directly to the grain size and roughness. On the other hand, it should be noted that, in this work, the oval form did not present a significant influence in the photocatalytic response, as it was stated in others reports.

The rate constant values obtained in this work can be compared with others reported from different deposition techniques, as it was mentioned before, we did not find reports about sputtered ZnO thin films applied for photocatalytic studies. As examples, it can be mentioned the following reports. ZnO thin films ~ 2.5 µm thickness were grown by sol-gel, exhibiting a maximum value of 0.297 h\(^{-1}\), in 4 h [20]. Other work about pyrolysis spray reported a \( k \) maximum value of 1.45 h\(^{-1}\), in 3 h [21]. ZnO films were grown by CBD on a 3 nm seed layer deposited by ALD, showed a \( k \) value of 0.258 h\(^{-1}\), in 4 h [22]. 1 µm ZnO films deposited by the hydrothermal technique were grown over a template (glass substrates with a sputtered layer of ZnO), obtaining a \( k \) value of 0.216 h\(^{-1}\), in 6 h [23]. From the above resume, it can be concluded that the degradation efficiencies

<table>
<thead>
<tr>
<th>Sample</th>
<th>( k (h^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO-50</td>
<td>0.1444</td>
</tr>
<tr>
<td>ZnO-200</td>
<td>0.2739</td>
</tr>
<tr>
<td>ZnO-400</td>
<td>0.6308</td>
</tr>
</tbody>
</table>

**Table 2.** Pseudo first order (\( k \)) rate constants for a molar concentration of \( 1.0 \times 10^{-5} \).

Fig. 5 shows the absorbance spectra of ZnO thin films. A decrease in the maximum absorption peak of MB can clearly be seen as the irradiation time increases. It can be observed the almost total MB degradation in a period of 5 h, under UV light irradiation for the ZnO-400 sample. The percentage degradations were of 51.8, 74.2, and 95.6 % for ZnO-50, ZnO-200 and ZnO-400, respectively. Using the data obtained from the aforementioned absorption spectra, the degradation kinetics was found, see Fig. 6. From the linear behavior of the plot a pseudo first-order kinetic model was confirmed. The pseudo first order rate constants are shown in Table 2.

**Fig. 5.** Absorption spectra of MB solution with 1.0 x 10-5 molar concentration. 1) ZnO-50, 2) ZnO-200 y 3) ZnO-400.

**Fig. 6.** Kinetics of degradation of ZnO thin films of a MB solution with molar concentration 1.0 x 10-5.
obtained in this work are competitive with other results reported in the scientific literature.

IV. CONCLUSIONS

ZnO films with different thicknesses were deposited by the sputtering technique. All films presented a wurtzite hexagonal structure with a preferential growth along the (002) planes. The microscopic analysis showed a uniform morphology with spherical grain shape for ZnO-50 and ZnO-400, and oval grain shape in the case of the ZnO-200 sample. Films exhibited an increase in the grain size with the film thickness. From AFM images and the Gwyddion software, the values of the roughness were estimated, obtaining similar values than others reported for films deposited by sputtering. The ZnO-400 film exhibited the highest photocatalytic efficiency to degrade the MB (95.6 %), and this is associated with the increase in thickness and not to the roughness or grain size.

Finally, the photocatalytic results obtained from ZnO films deposited by the sputtering technique show that the ZnO thin films are a viable alternative for degrading MB.

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