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Article

# Spray Pyrolysis Synthesis of Pure and Mg-Doped Manganese Oxide Thin Films

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**Abstract:** Pure and Mg-doped manganese oxide thin films were synthesized on heated glass substrates using the spray pyrolysis technique. The surface chemical composition was investigated by the use of X-ray photoelectron spectroscopy (XPS). Structural and morphological properties were studied by using X-ray diffraction (XRD), scanning electron microscope (SEM) and atomic force microscopy (AFM). Optical properties were characterized by UV-visible spectroscopy. XPS spectra showed typical Mn (2p<sub>3/2</sub>), (2p<sub>1/2</sub>) and O (1s) peaks of Mn<sub>3</sub>O<sub>4</sub> with a slight shift attributed to the formation of different chemical states of manganese. XRD analysis revealed the tetragonal phase of Mn<sub>3</sub>O<sub>4</sub> with a preferred (211) growth orientation that improved with Mg-doping; likewise, grain size is observed to increase with the Mg doping. SEM images of Mn<sub>3</sub>O<sub>4</sub> films showed rough surfaces composed of uniformly distributed nanograins whose size decreases with the Mg-doping. The manganese oxide films surface observed in AFM show a textured, rough and porous surface. The combination of transmittance and absorption data in the UV-visible range allowed determining the energy values of the Eg band gap (1.5–2.5 eV). The decrease of the band gap with the Mg-doping increase is attributed to the influence of the greater size of the Mg<sup>2+</sup> ion in the manganese oxide lattice.

**Keywords:** MnO; XPS; AFM; nanograins; spray pyrolysis



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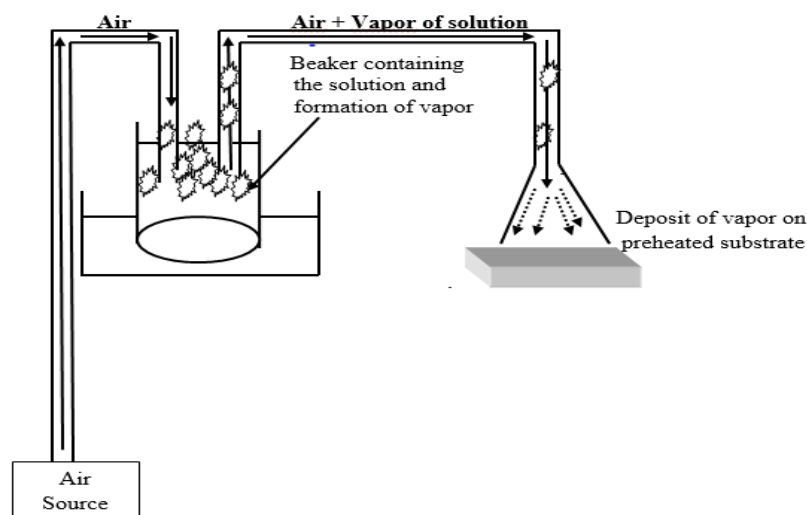
## 1. Introduction

Oxides in nanometric films have received increasing interest to the potential applications that derive from their interesting electrical, magnetic and catalytic properties. Manganese oxides in nanometric films are intriguing compounds possessing excellent electrochemical activity allowing it to be used in electrochemistry applications. Due to the three Mn<sup>2+</sup>, Mn<sup>3+</sup> and Mn<sup>4+</sup> different oxidative states of manganese, the manganese oxide compound exists in four structures (MnO, Mn<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>) [1], which all present interesting physical and chemical properties as important as those of the metal oxides materials (ZnO, SnO<sub>2</sub>, NiO, CuO, . . . ) belonging to the transparent conducting oxides (TCO) family. Manganese oxide thin films are well suited for various applications such as in optoelectronic applications for their use in solar energy conversion [2,3], electrochemical capacitors [4,5], batteries, sensors [6], chemical sensors [7,8], magnetoelectronic devices, electrochemical energy storage devices and catalytic activity [9–11]. Quality manganese oxide thin films are relatively easy to prepare, with many physical and chemical techniques such as atomic layer deposition [12], co-precipitation [13], sputtering [14], Molecular Beam Epitaxy [15], chemical vapor deposition [16] and spray pyrolysis [17,18]. It has been shown earlier [19,20] that, amongst these techniques, spray pyrolysis presents many advantages:

it is cheaper and easier to implement, while allowing for obtainment of homogeneous coatings on large areas. Furthermore, it is easy to obtain metals-doped films by simply adding some other solution(s) to the primary one. In this work, we synthesize and characterize pure and Mg-doped manganese oxide thin films using spray pyrolysis but in order to obtain oxide thin films of good quality, it is necessary to control efficiency the phase formation, the grain size, the shape and morphologies of nanometric films. It is well known that these parameters have great influence on the physical properties and applications of oxides in nanometric films. This paper allowed us to review the synthesis of manganese oxides films with various Mg-doping for photocatalytic properties study which will be applied in industrial waste from textile factories.

## 2. Materials and Methods

Pure and doped manganese oxide thin films were deposited onto heated glass substrates using the spray pyrolysis technique. The primary solution permitting to obtain pure manganese oxide was prepared with 0.1 M manganese chloride ( $\text{MnCl}_2, 6\text{H}_2\text{O}$ ) in 100 mL deionized water. A secondary solution prepared from magnesium chloride hexahydrate ( $\text{MgCl}_2, 6\text{H}_2\text{O}$ ) was added for the Mg-doping to the primary solution at various concentrations ((Mg/Mn) ratio: 3%, 5%, 7% and 9%). These solutions were sprayed onto heated glass substrates maintained at 350 °C during the deposit time. Figure 1 schematically illustrates the principle of the pyrolysis method used in this study.



**Figure 1.** Schematic diagram of the used spray pyrolysis technique.

The obtained pure and Mg-doped samples were characterized by techniques adapted to thin films analysis. X-ray photoelectron spectroscopy (XPS-K-alpha apparatus from Thermo Scientific Instruments, Waltham, MA, USA) and X-ray diffraction (XRD-X'Pert PRO from PANalytical (Malvern, UK) utilizing copper line of wavelength  $\lambda = 1.54 \text{ \AA}$ ) were used for chemical compositional analysis, and structural study, respectively. Microstructural and morphological characterizations were obtained by scanning electron microscopy (SEM JEOL 7500-F Instrument, Tokyo, Japan) and atomic force microscopy (AFM-Dimension Edge from Bruker, Bruker, MA, USA), respectively. The materials band gap energy ( $E_g$ ) is calculated using the Tauc's plot, combining absorption and transmittance data extracted from UV-visible (Specord 50 plus spectrophotometer, Analytik Jena, Jena, Germany) analysis.

## 3. Results

### 3.1. XPS Compositional Analysis

XPS survey spectra are used to investigate the chemical composition and the valence states of manganese and oxygen for the pure and Mg-doped manganese oxide films

(Figure 2). Carbon is the sole contaminant with some traces of nickel detected on the films' surface; the other peaks that appear in the spectra are attributed to the core levels of the O and Mn elements; traces of the magnesium dopant were detected from their Mg (1s) core level. The principal Mn (2p<sub>3/2</sub>), (2p<sub>1/2</sub>) and O (1s) core levels are shown in Figure 3. Binding energy shifts of the Mn (2p) and O (1s) peaks are listed in Table 1; they present an average half-eV oscillation, probably due to the formation of different chemical states of the Mn and resulting into the formation of mixed oxides (MnO, Mn<sub>3</sub>O<sub>4</sub>). Indeed, as reported by Li et al. [21], the Mn (2p<sub>3/2</sub>) peak that appears around 640.0 eV is attributed to Mn<sup>2+</sup> cations, whereas peaks detected in the energy range 641.0–642.0 eV are assigned to Mn<sup>3+</sup> and Mn<sup>4+</sup>, respectively. In the present work, the binding energies are recorded at 640.4 eV for the pure films and vary from 641.0 to 641.5 eV for the Mg-doped films. This is consistent with the pure films corresponding to the growth of the MnO compound, while the Mg-doped films show the formation of Mn<sub>3</sub>O<sub>4</sub>.

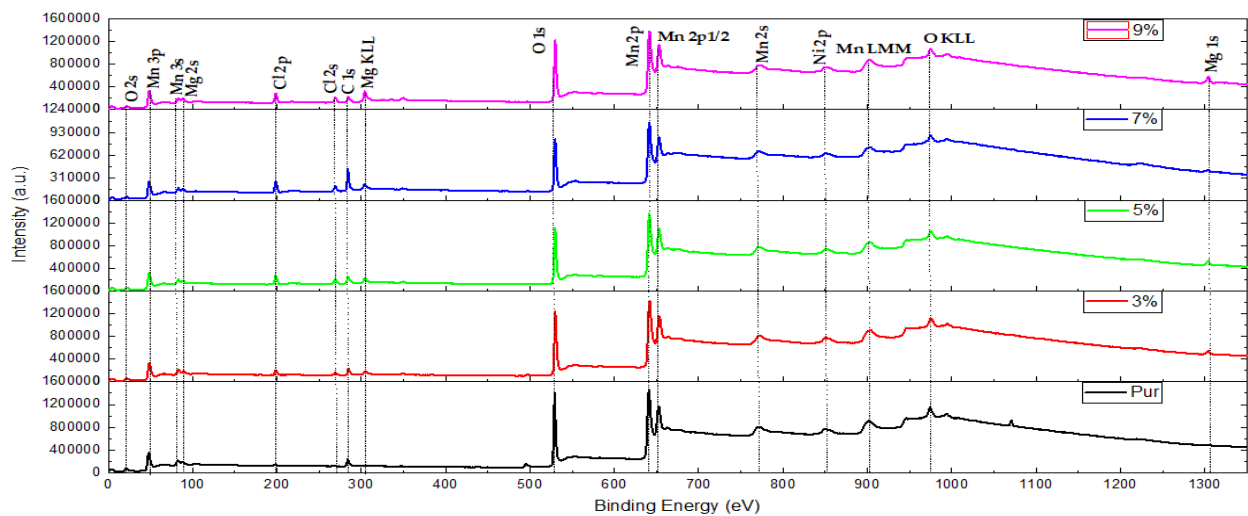


Figure 2. XPS survey spectra of the pure and Mg-doped manganese oxide thin films.

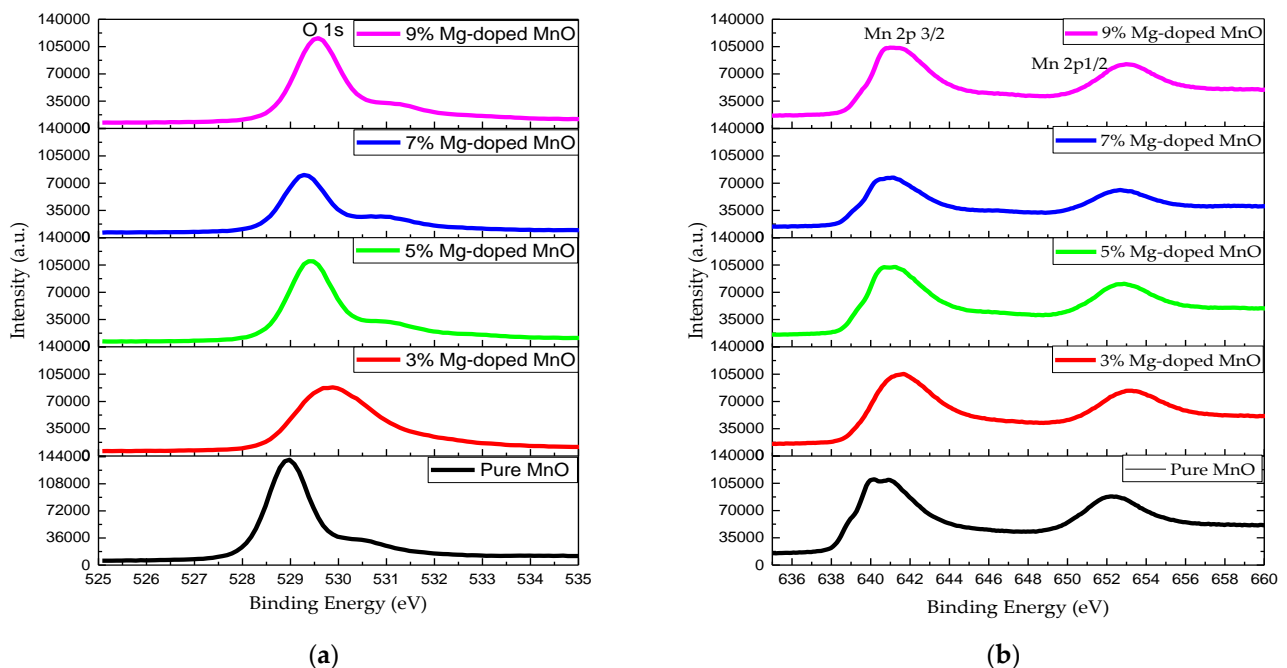
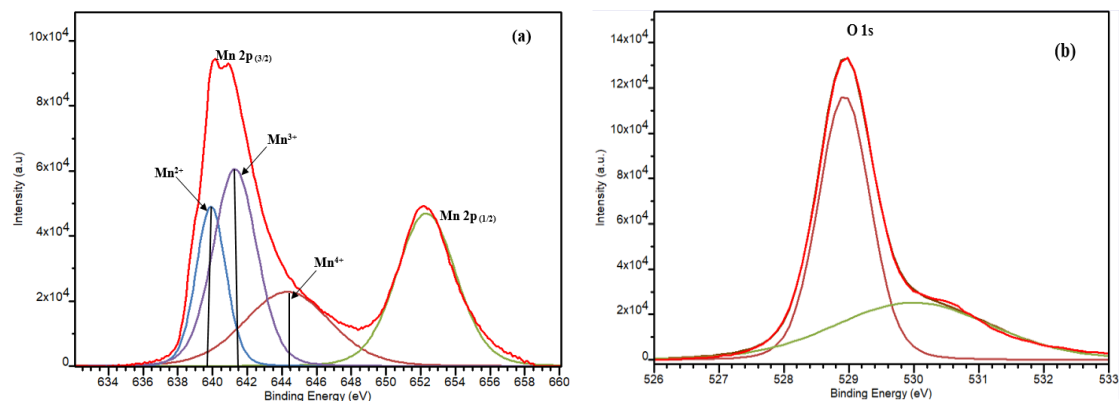


Figure 3. XPS spectra of the most intense core levels peaks of manganese (b) Mn (2p) and oxygen (a) O (1s).

**Table 1.** XPS determined binding energies of the most intense O and Mn elemental peaks.

Samples	O (1s) Binding Energy (eV)	Mn (2p3/2) Binding Energy (eV)	Mn (2p1/2) Binding Energy (eV)
Pure MnO film	529	640.4	652.4
3% Mg-doped film	529.9	641.5	653.5
5–7% Mg-doped film	529.5	641.0	653.0
9% Mg-doped film	529.7	641.5	653.6

The oxygen peak is decomposed into two distinct components (Figure 3a): the first one appears at 529 eV and is due to Mn–O bonds. The other less intense oxygen peak positioned at 530.6 eV is related to contaminant molecules loosely bound the surface. The curve-fitted XPS spectra (Figure 4) of the Mn (2p) core levels suggest in fact that the 2p3/2 peak is composed of a doublet, with one component at 639.5 eV and the other one at 641.5 eV. This confirms the presence of two different valences, Mn<sup>2+</sup> and Mn<sup>3+</sup>, highlighting the growth of two MnO and Mn<sub>3</sub>O<sub>4</sub> compounds. A larger and less intense component appears at 644.4 eV; it is due to the presence of the Mn<sup>4+</sup> state of manganese.

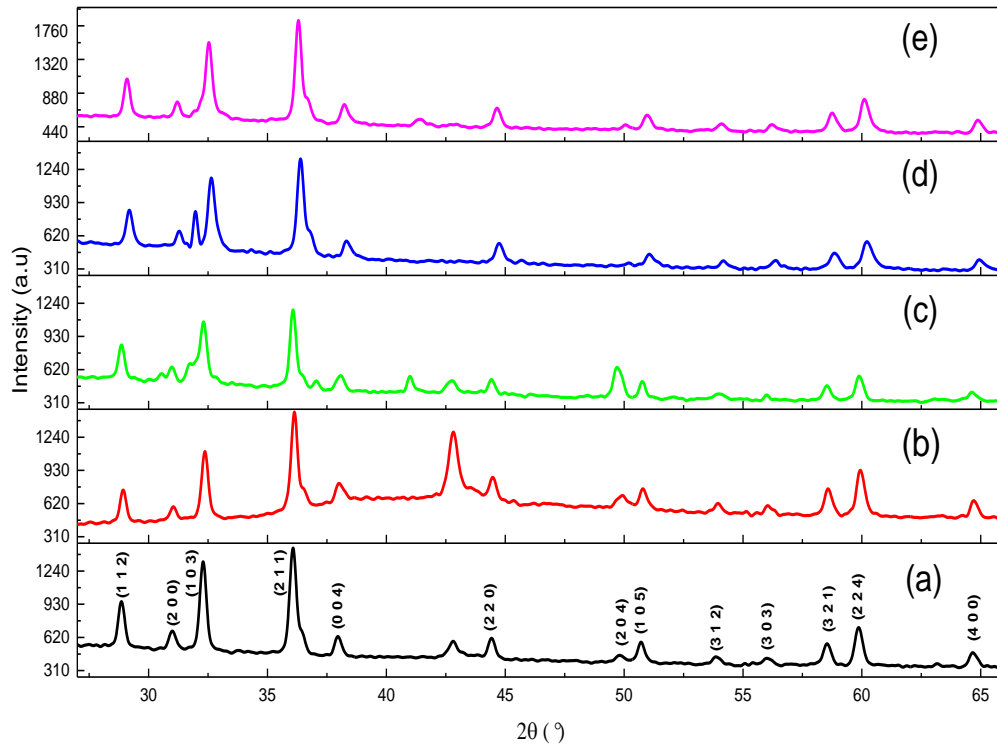
**Figure 4.** Curve-fitted XPS spectra: (a) Mn (2p3/2) and Mn (2p1/2) peaks (b) O (1s) core level.

The transitions of XPS spectra of MnO compound are strongly dependent on the valence of the manganese (Mn<sup>2+</sup>, Mn<sup>3+</sup>, Mn<sup>4+</sup>). They are discussed and reported by Ilton [22,23] and Cerato [24,25].

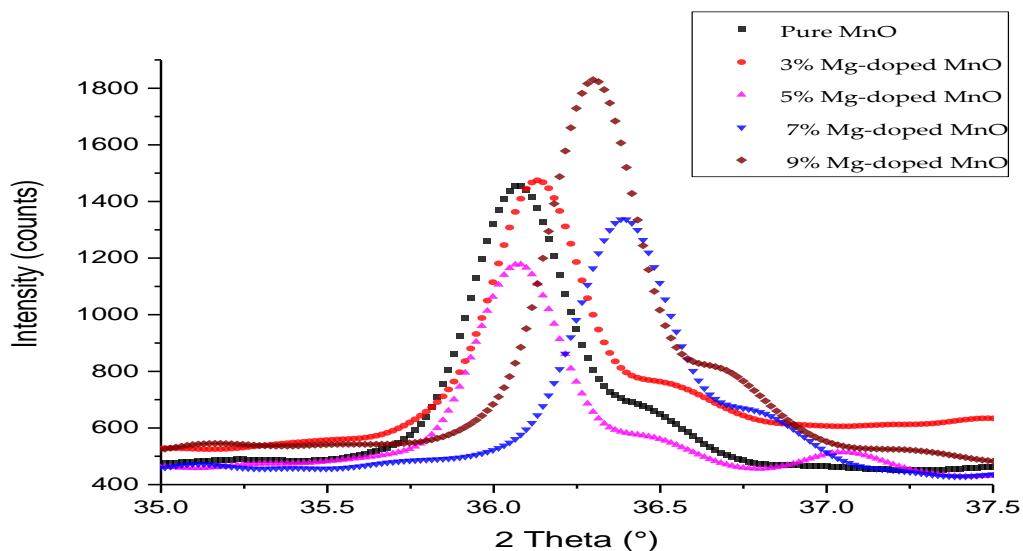
### 3.2. XRD Characterization

Figure 5 shows the XRD patterns of the deposited pure and Mg-doped thin films. Fourteen peaks of different intensities are resolved with the principal (112), (103) and (211) indexed planes, corresponding to 2θ diffraction angles around 28°, 32.5° and 36.5°. These peaks are the mostly shown and discussed in [26–28], and, with reference to the JCPDS cards No. 80–0382 and 00-024-0734, they do confirm the presence of the tetragonal Mn<sub>3</sub>O<sub>4</sub> phase. The intensity of the indexed plane (211) increases with the increase of Mg doping and is particularly pronounced for 7% and 9% doping. It results also in diffraction peak shift. This indicates that the films grow preferentially along the (211) direction and confirms the crystallization improvement of the films under the Mg-doping effect. Figure 4b shows increased diffraction peak at around 43°, which does not appear on the other spectra; it is probably due to a faulty placement of the sample. On the other hand, the position of this peak is unstable and shifts to the left and to the right, as observed on XPS spectra (Table 1, Figure 6). These oscillations are attributed to the presence of two (Mn<sup>2+</sup>, Mn<sup>3+</sup>) valence types confirming the formation of a mixed oxide (MnO/Mn<sub>3</sub>O<sub>4</sub>). Similar behaviors were observed on the XRD spectra of Sr doped-ZnO [29] and were attributed to a size effect between Zn<sup>2+</sup> and Sr<sup>2+</sup> ions. If we compare the ionic radii of the Mn<sup>2+</sup> (1.17 Å), Mn<sup>3+</sup> (0.66 Å) and Mn<sup>4+</sup> (0.60 Å) ions and of Mg<sup>2+</sup> (0.66), it is only the Mn<sup>2+</sup> ion that can explain the shift of

the XPS and DRX peaks. The void resulting from the ratio  $r_{\text{Mn}^{2+}}/r_{\text{Mg}^{2+}} = 1.77$  is expected to destabilize the crystallographic structure of the Mn-O film, which would cause the observed perturbations of the peak intensities (positions) in the XRD (and XPS) measurements.



**Figure 5.** X-ray diffraction patterns of pure and Mg-doped Mn-O thin films. (a): Pure MnO; (b): 3% Mg-doped MnO; (c): 5% Mg-doped MnO; (d): 7% Mg-doped MnO; (e): 9% Mg-doped MnO.



**Figure 6.** Shift of the position of (211) diffraction peak as measured of the five different deposited films.

The  $a$ ,  $b$  and  $c$  tetragonal lattice parameters were determined from the XRD spectra. The tetragonal structure is defined by  $a = b \neq c$  and the interplanar spacing  $d$  is a function

that is dependent on  $a$ ,  $b$  and  $c$  and on the indexed diffraction peaks ( $hkl$ ) as shown in the following relation:

$$\frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2}, \quad (1)$$

The interplanar spacing  $d$  can also be determined from Bragg's law below:

$$2d\sin\theta = n\lambda, \quad (2)$$

where  $d$  is the interplanar spacing,  $\theta$  is the Bragg diffraction angle,  $n$  is the order of diffraction (usually  $n = 1$ ) and  $\lambda$  is the X-ray wavelength.

By combining Equations (1) and (2) and applying them to the (211) and (103) most intense peaks, one easily calculates the  $a$  and  $c$  lattice parameters that are listed in the following Table 2.

**Table 2.** Determination of the  $a$  and  $c$  lattice parameters for the five different deposited films.

Sample	$2\theta$ (°)	( $hkl$ )	$d$ (Å)	$a = b$ (Å)	$c$ (Å)	$a = b$ (Å) in Literature	$c$ (Å) in Literature
Pure MnO	32.29	103	2.770	5.7643	9.4757	8.135 [30]	9.28 [30]
	36.08	211	2.488			5.752 [31]	9.47 [31]
MnO (3% Mg)	32.36	103	2.763	5.7565	9.4517	—	—
	36.13	211	2.484				
MnO (5% Mg)	32.29	103	2.770	5.7647	9.4766	—	—
	36.07	211	2.487				
MnO (7% Mg)	32.65	103	2.740	5.7166	9.3677	—	—
	36.39	211	2.466				
MnO (9% Mg)	32.53	103	2.751	5.7302	9.4041	—	—
	36.31	211	2.472				

By using the Debye–Scherrer Equation (3) that is extensively used with more details by Borchert et al. [32], the average Mn-O crystallite size may be estimated according to:

$$D = \frac{0.9\lambda}{\beta(2\theta)\cos\theta}, \quad (3)$$

where  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg diffraction angle and  $\beta$  is the broadening of the diffraction peak measured at half of its maximum intensity.

The defects density in the synthesized Mn-O films defined as the length of dislocation lines per unit volume of the crystal can be estimated by the use of the following Equation (4):

$$\delta = \frac{1}{D^2} \quad (4)$$

where  $D$  is the average Mn-O crystallite size determined from Equation (3).

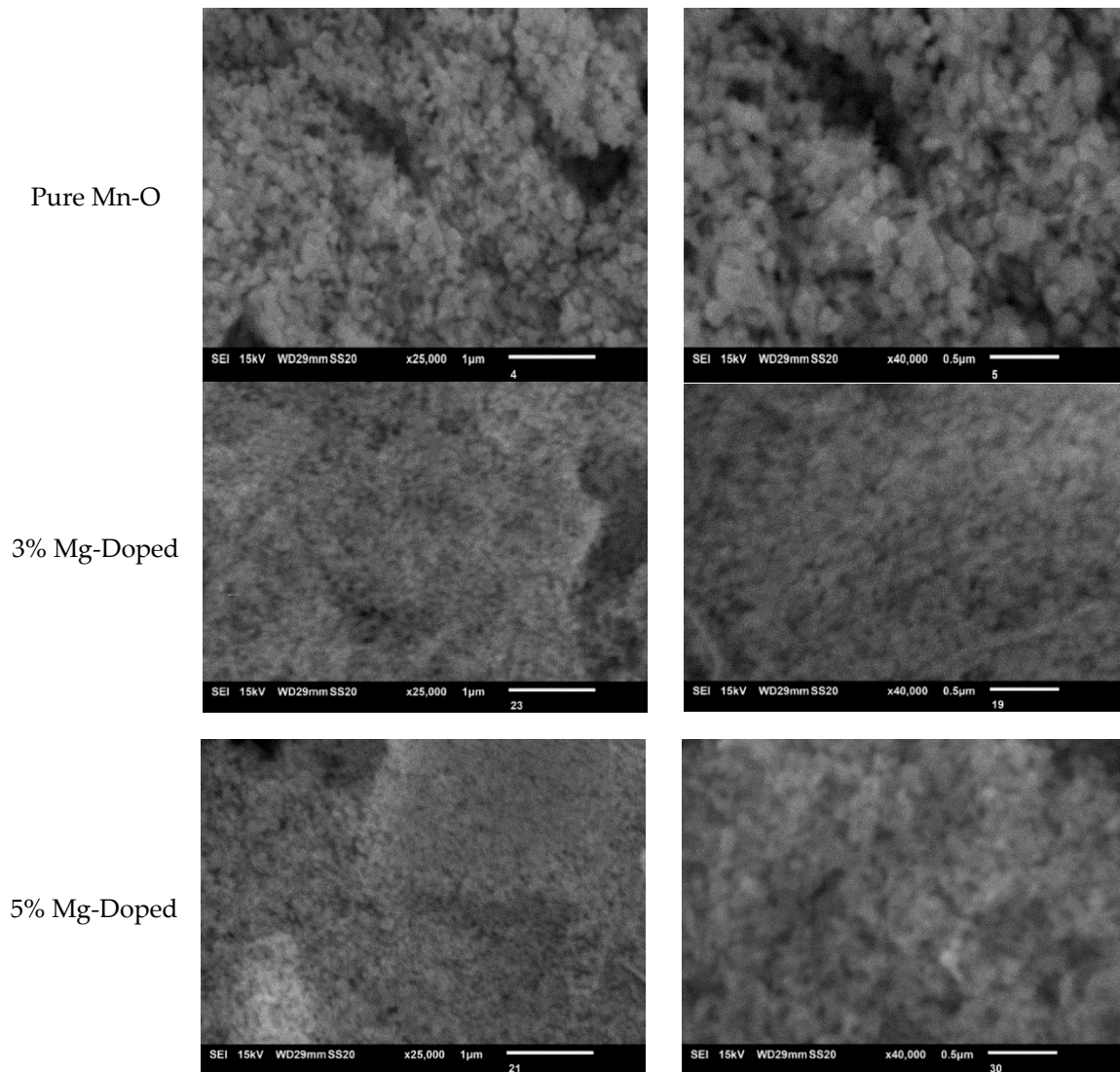
By application of Equations (3) and (4) to the intense diffraction peak (211) for the pure and Mg-doped Mn-O, the determined values of  $D$  and  $\delta$  are shown in Table 3.

**Table 3.** Determination of the average crystallite size  $D$  and defects density  $\delta$  for the five different thin films.

Sample	$2\theta$ (°)	$\theta$ (°)	$d_{(211)}$ (Å)	$\beta$ (°)	$D$ (nm)	$\delta$ ( $10^{-3}$ )
Pure MnO	36.08	18.04	2.488	0.3354	24.9075	1.6119
MnO (3% Mg)	36.13	18.06	2.484	0.3088	27.0534	1.3663
MnO (5% Mg)	36.07	18.03	2.487	0.2844	29.3722	1.1591
MnO (7% Mg)	36.39	18.19	2.466	0.3624	23.0756	1.8779
MnO (9% Mg)	36.31	18.15	2.472	0.3095	27.0081	1.3709

### 3.3. SEM and AFM Analysis

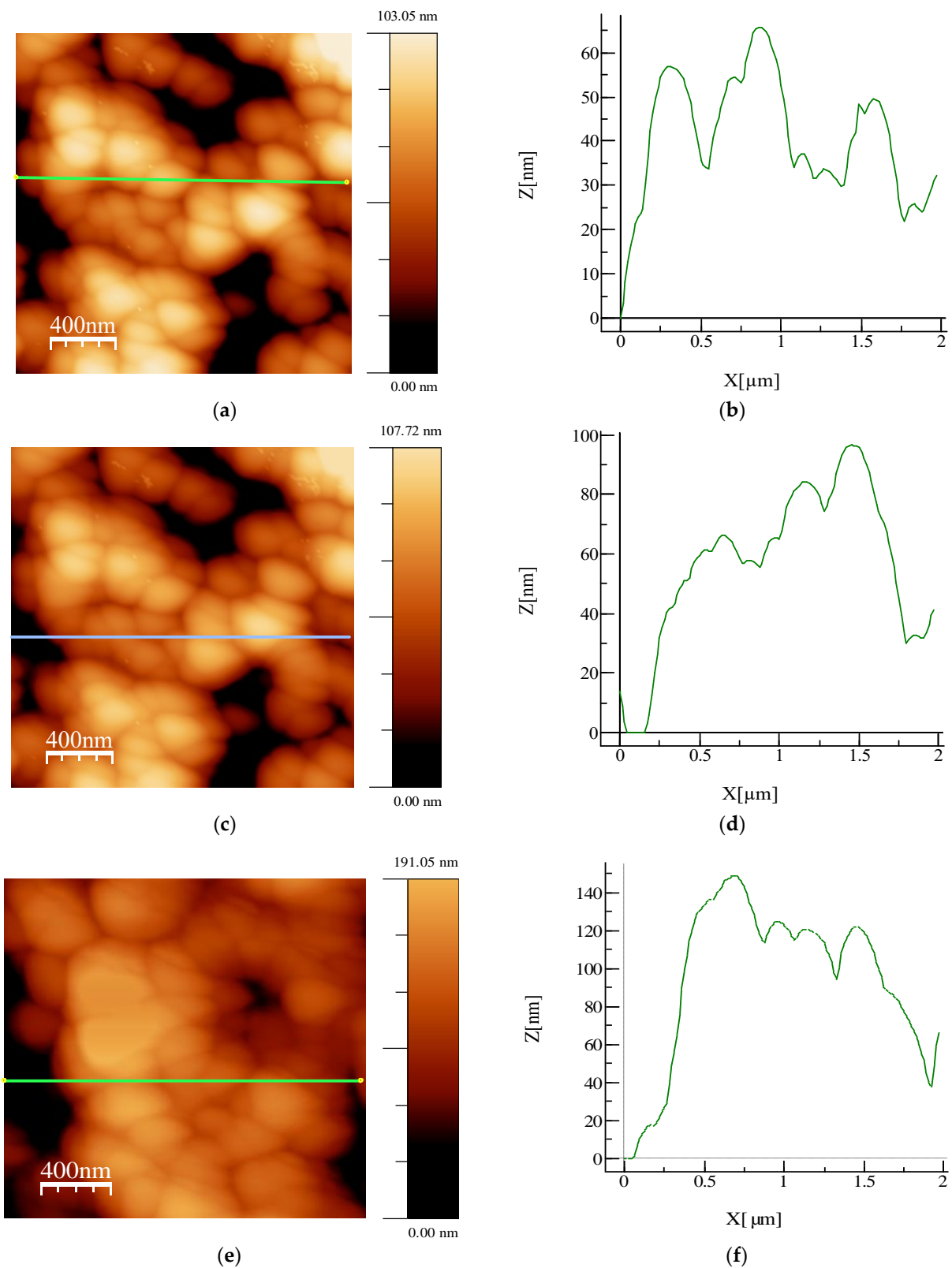
The morphologies of the different Mn-O films recorded by SEM are shown in Figure 7 (magnification  $\times 40,000$ ). Morphological changes in MnO are clearly linked to variations in the Mg-doping from 3% to 9%: the Mg-doping appears to have an effect on the surface roughness with the pure MnO surface composed of larger grains, appearing rougher than other Mg-doped surfaces.



**Figure 7.** SEM images of pure and Mg-doped Mn-O oxide recorded at a magnification  $\times 40,000$  (1 and 0.5 scales are shown).

The Mg-doping effect on the topography of the films' surfaces is confirmed by Atomic Force Microscope (AFM) (Figure 8) using the tapping mode in  $2 \mu\text{m} \times 2 \mu\text{m}$  areas. It is observed that the MnO deposit is not homogeneous but formed by grains aggregated in "egg" shaped forms. The black areas represent the glass substrate showing the formation of MnO porous nanoflakes. As shown by the profiles taken on a horizontal line on each image, the aggregation of the grains increases with the increase of the Mg-doping. The calculated average rms roughness on this line is 50 nm for the pure MnO, 80 nm for 3% Mg doped-MnO and 130 nm for the 5%–7% Mg doped-MnO.





**Figure 8.** AFM images of pure and Mg-doped Mn-O oxide: (a,c,e) Surface morphology for pure, 3% and 5% Mg-doped Mn-O oxide. (b,d,f) surface profiles measured along the horizontal lines shown on the corresponding AFM images.

These AFM observations diverge a little from those obtained in SEM. We suggest this may be due to the fact that the SEM technique takes into account the contribution of the

microstructures of the subsurface layers, whereas AFM is probing exclusively the extreme surface of the films.

### 3.4. Optical Measurements

The transmittance (T) or absorbance ( $\alpha$ ) optical properties of the MnO samples were determined by using UV-visible spectrometry in a double beam spectrophotometer. T and  $\alpha$  spectra were recorded in the 200–900 nm range as shown in Figure 9. It appears that the transmittance is less than 50% for all samples; as a result, the synthesized films are clearly not so transparent: this is attributed to the inhomogeneity of the deposit as shown by the AFM analysis. The transmittance is varying from 30% to 15% for pure manganese oxide and to 9% for the Mg-doped Mn-O films; thus, the Mg doping reduces greatly the samples transparency.

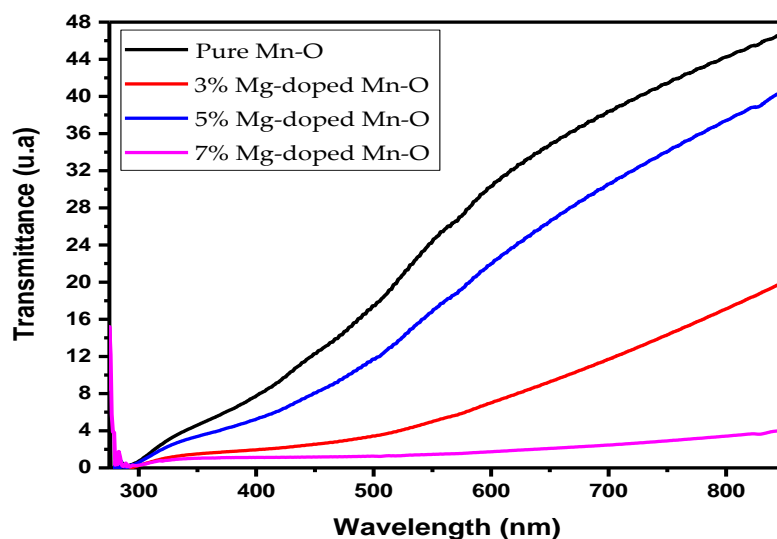


Figure 9. Transmittance spectra of the pure and Mg-doped Mn-O films.

By combining the transmittance and absorption data, the value of the MnO energy gap is calculated from the Tauc's plot [32], using the equation:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5)$$

where  $\alpha$  is the absorption yield,  $h\nu$  is the photon energy,  $A$  is a constant and  $E_g$  is the band gap energy.

A typical plot of  $(\alpha h\nu)^2$  versus  $(h\nu)$  is shown in Figure 10. According to Equation (5), the extrapolation on Figure 10 of the linear portion of the curve to  $(\alpha h\nu)^2 = 0$  gives the  $E_g$  band gap values listed in Table 4. They are found to be in between 1.4–2.5 eV, with the band gap decreasing with the increase of Mg-doping. As interpreted in earlier paragraphs, this may be due to the greater ionic radius of  $Mg^{2+}$  ions compared to the  $Mn^{2+}$  ones. The insertion of  $Mg^{2+}$  in the  $Mn^{2+}$  sites creates defects resulting from the distortion in the MnO lattice. The decrease in band gap with doping can be also linked to the presence of voids formed by the magnesium ions substituting the manganese ones in the host lattice. Similar results have been observed in Mg and Ga co-doped ZnO and in molybdenum-doped indium oxide thin films [33,34]. In general, the band gap values obtained in this study for pure and Mg-doped samples are in the range of those reported in the literature [35–38].

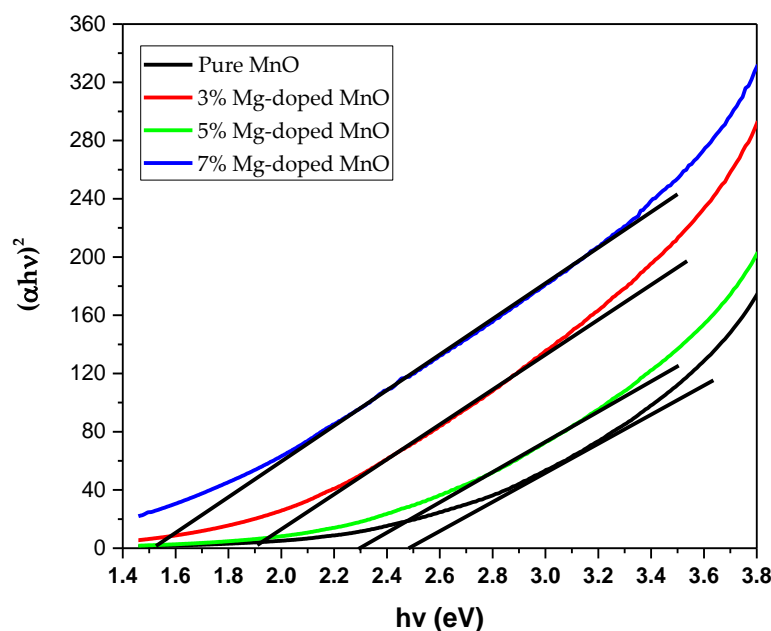


Figure 10. Eg band gap energy extracted from the Tauc's plot for the different deposited films.

Table 4. Effect of Mg-doping on Eg values.

Sample	Eg (eV)
Pure MnO	2.5
3% Mg-doped MnO	1.9
5% Mg-doped MnO	2.3
7% Mg-doped MnO	1.5

#### 4. Conclusions

This report studied the chemical composition, the structural, morphological and optical properties of  $\text{Mn}_3\text{O}_4$  films deposited on glass substrate heated at 350 °C by spray pyrolysis. XPS characterization highlighted the chemical composition of  $\text{Mn}_3\text{O}_4$  films. XRD analysis evidenced the  $\text{Mn}_3\text{O}_4$  polycrystalline phase in a tetragonal structure with an intense diffraction plane (211), the preferred growth orientation along this direction. SEM images showed a rough surface for  $\text{Mn}_3\text{O}_4$  films with is improved with the Mg-doping increase. AFM showed textured surface formed by nanograins shaped like an “egg”. UV-visible spectroscopy revealed a transmittance yield ranging between 15–30%. This low yield is probably due to the porosity of the surface. The Eg band gap energy determined from Tauc plots (2.0–3.3 eV) are in accordance with those of the literature. The results of this study are going to be used for further characterization of photocatalytic properties for application in industrial waste treatment.

**Author Contributions:** M.G. proposed, designed the study and wrote the paper; M.A.D. performed the experiments; S.E.N., C.F., and D.T. contributed to the interpretations of the results and paid the invoice of the publication charge; J.-J.P. supervised and commented the final article version; A.B. discussed some results. In general, all authors contributed to the discussion and interpretation of the results. All authors have read and agreed to the published version of the manuscript.

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