



Ultrasonic spray pyrolysis growth of ZnO and ZnO:Al nanostructured films: Application to photocatalysis



G. Kenanakis ^{a,b,*}, N. Katsarakis ^{a,b}

^a Institute of Electronic Structure and Laser, Foundation for Research & Technology – Hellas, P.O. Box 1385, Vassilika Vouton, 711 10 Heraklion, Crete, Greece

^b Center of Materials Technology and Photonics, School of Applied Technology, Technological Educational Institute of Crete, 710 04 Heraklion, Crete, Greece

ARTICLE INFO

Article history:

Received 7 January 2014

Received in revised form 1 September 2014

Accepted 19 September 2014

Available online xxx

Keywords:

A. Oxides

A. Semiconductors

A. Nanostructures

A. Thin films

B. Chemical synthesis

D. Catalytic properties

ABSTRACT

Pure and Al-doped ZnO (Al = 1, 3, 5%) nanostructured thin films were grown at 400 °C on glass substrates by ultrasonic spray pyrolysis, a simple, environmental-friendly and inexpensive method, using aqueous solutions as precursors. The structural and morphological characteristics of the samples depend drastically on deposition parameters; ZnO nanostructured films, nanopetals and nanorods were systematically obtained by simply varying the precursor solution and/or the spraying time. Transmittance measurements have shown that all samples are transparent in the visible wavelength region. Finally, the photocatalytic properties of the samples were investigated against the degradation of stearic acid under UV-A light illumination (365 nm); both pure and Al-doped ZnO nanostructured thin films show good photocatalytic activity regarding the degradation of stearic acid, due to their good crystallinity and large surface area.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

In the last years, heterogeneous photocatalysis has re-attracted extensive interest for the degradation of organic pollutants [1–6] and the production of self-cleaning [7–8] or anti-bacterial surfaces [9]. Up to now, great attention has been given to fine metal oxide powders, in particular TiO₂ and ZnO, since high photocatalytic efficiency can be achieved by increasing the effective surface area of the materials [10]. However, these powders have mostly been used in water suspensions, thus limiting their practical use due to difficulties in their separation and recovery. Supporting photocatalytic materials on a steady substrate can eliminate this issue. Many thin film deposition techniques have been widely used for the immobilization of TiO₂ and ZnO [11–12].

Compared to other deposition techniques, spray pyrolysis offers several advantages like non-vacuum use of inexpensive equipment, ease of large-scale adoption and possibility of automation for industrial use. Moreover, it can offer control of the basic characteristics of the as-grown samples through the deposition conditions, such as substrate temperature, type and concentration of precursor solution, type and pressure of the carrier gas,

geometric characteristics of the spraying system and spraying rate [13–15].

In this work, we investigate the influence of precursor type, deposition time and Al doping concentration on the morphological, structural, and optical characteristics of pure and aluminum doped ZnO samples, which were deposited using the ultrasonic spray pyrolysis (USP) on Corning glass substrates at 400 °C. Furthermore, emphasis is given on the photocatalytic activity of the as-grown pure and Al-doped ZnO samples against the degradation of stearic acid under UV-A light illumination (365 nm). We provide evidence that both ZnO and ZnO:Al nanostructured thin films deposited by USP, show high photocatalytic activity, which may open new horizons in large-scale ZnO photocatalytic applications.

2. Experimental details

2.1. Deposition of pure and Al-doped ZnO nanostructured thin films

ZnO nanostructured thin films were grown by the ultrasonic spray pyrolysis technique [16] on Corning glass square inch substrates (Corning Eagle 2000 Borosilicate Glass, Specialty Glass Products) for various deposition times using 0.5 M precursor solutions of: (a) zinc acetate (Zn(CH₃COO)₂·2H₂O) and (b) zinc nitrate (Zn(NO₃)₂·6H₂O) in ultrapure water (18.2 MΩ cm), after stirring for 15 min at 25 °C. Before deposition, the substrates were cleaned for 10 min using a piranha solution (H₂SO₄/H₂O₂ = 3/1),

* Corresponding author at: Institute of Electronic Structure and Laser, Foundation for Research & Technology – Hellas, P.O. Box 1385, Vassilika Vouton, 711 10 Heraklion, Crete, Greece. Tel.: +30 2810391917.

E-mail address: gkenanak@iesl.forth.gr (G. Kenanakis).

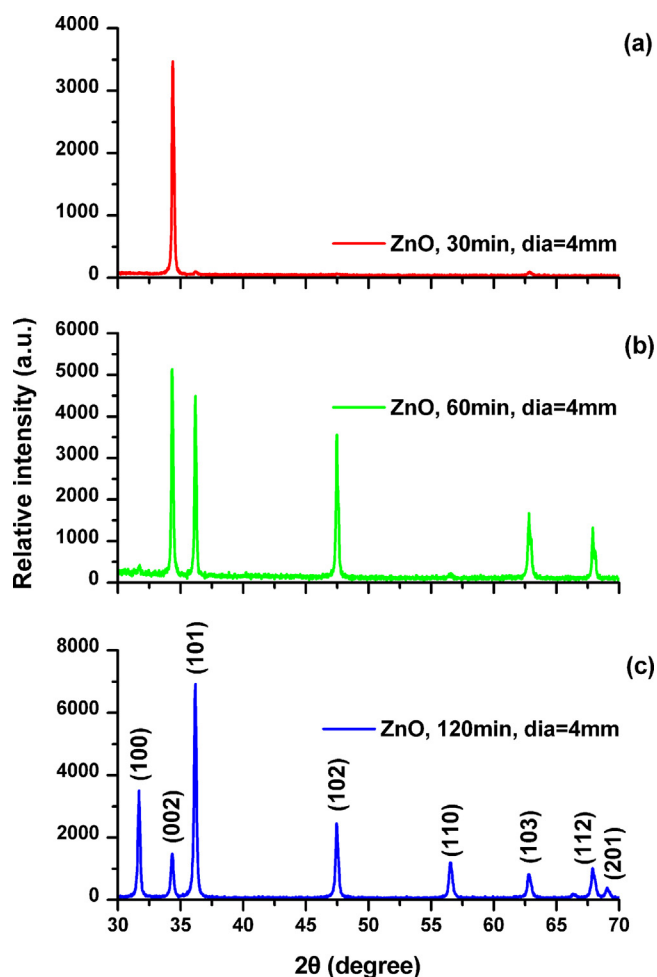


Fig. 1. X-ray diffraction patterns of ZnO samples deposited by the USP technique for (a) 30, (b) 60 and (c) 120 min, using a 0.5 M zinc acetate precursor and a 4 mm diameter nozzle, at 400 °C.

rinsed with ultrapure water and dried under N₂ gas flow. The deposition was performed at 400 °C by an ultrasonic particle generator (Model 241 PG, Sonaer Inc.), using a ~0.6 bar N₂ flow and a frequency of 2.4 MHz allowing 100% particle generation. The spraying conditions were optimized before deposition, the respective values chosen to be: 4 mm and 8 mm nozzle diameter, 3.5 cm nozzle length and 5 cm distance between nozzle and substrate. The average diameter of the misted droplet was approximately calculated from an expression given by Lang [17]:

$$D_d = 0.34 \left(\frac{8\pi\gamma}{\rho f^2} \right)^{1/3}$$

where D_d is the droplet diameter, γ is the solution surface tension, ρ is the solution density and f is the applied ultrasonic frequency. The diameter of the misted droplets in our experiment was calculated using the above expression and was found to be around 2.3 μm.

Regarding the Al-doped ZnO samples, these were deposited using the same experimental conditions mentioned above, employing as precursor a 0.5 M solution of zinc acetate and aluminum nitrate (Al(NO₃)₃·9H₂O) in ultrapure water. The nominal % molar concentration of Al in the precursor solution was 1, 3 and 5%, respectively. After growth, all samples were thoroughly washed with ultrapure water, and dried in air.

2.2. Characterization techniques

The crystal structure of the pure and Al-doped ZnO samples was determined by X-ray diffraction (XRD) using a Rigaku (RINT 2000) diffractometer with Cu Kα ($\lambda = 1.5406$ Å) X-rays, while their surface morphology was studied by means of a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F) and an atomic force microscope (AFM) in tapping mode (Digital Instruments – Nanoscope IIIa). The surface roughness (RMS) of the pure and Al-doped ZnO thin films was determined using the scanning probe image processor (SPIP, v. 3.3.5.0) image processing software for nano- and micro-scale microscopy from Image Metrology. Finally, UV–vis transmittance spectra of the samples were recorded using a PerkinElmer (Lambda 950) spectrophotometer over the wavelength range of 250–1100 nm, while their thickness was measured using a stylus profilometer (Alpha-step 100, Tencor).

2.3. Photocatalytic activity study

There are many different methods that can be used to determine the activity of photocatalytic surfaces. Popular techniques include those based on the photo-oxidation of organic films such as stearic acid [18–23] or organic vapors [24] and contact angle changes [25].

The photocatalytic activity of our pure and Al-doped ZnO samples was determined using stearic acid (SA) as a model compound, in which a thin layer of SA is deposited onto the film and its photocatalytic destruction is monitored as a function of time [18–23]. This method has gained preference over the years since SA provides a reasonable model compound for solid films that deposit on exterior and interior surfaces. Moreover, SA is very stable under UV illumination in the absence of a photocatalyst film (phenomenon of photolysis). Furthermore, SA can be easily laid down from a methanol or chloroform solution making the test much easier.

In order to deposit SA on the ZnO nanostructured thin films, a 0.1 M SA solution in chloroform was spin-coated on the sample surface under test at a rotation speed of 500 rpm for 30 s. Samples were then dried at 80 °C in air for 10 min.

The decomposition of SA can be demonstrated by FT-IR spectroscopy through the monitoring of the asymmetric C–H stretching mode of the CH₃ group at 2958 cm^{−1} and the asymmetric and symmetric C–H stretching modes of the CH₂ group at 2923 and 2853 cm^{−1}, respectively. The photocatalytic activity experiments on all ZnO samples for the decomposition of SA were performed at ambient temperature. It is worth mentioning that all photocatalytic activity tests were carried out for at least five times on our Al_yZn_{1−y}O ($y = 0.00, 0.01, 0.03, 0.05$) samples in order to examine their stability under UV-A light illumination, demonstrating no changes in the photocatalytic activity after five runs. The integrated area of the SA C–H stretching peaks (2800–3000 cm^{−1}) was monitored using a Fourier transform infrared spectrometer (FT-IR, IRPrestige-21, Shimadzu) before and after black light illumination in a box reactor at certain time intervals. The light source used was a HPK 125 W Philips mercury lamp with main emission wavelength at 365 nm and an incident light intensity of 8.9 mW/cm². For ease in comparison of the photocatalytic activity between different samples, the integrated area of the C–H stretching peaks (2800–3000 cm^{−1}) measured at each irradiation time interval was normalized to the initial integrated area (prior to the irradiation) in order to calculate the percentage of SA remaining as a function of irradiation time. Blank experiments (photolysis) were also performed using bare Corning 7059 Borosilicate substrates (glass, free of ZnO) under exactly the same conditions as used for the ZnO samples. Finally, the SA disappearance rate (mol/min) and the formal quantum efficiency (FQE) for all ZnO samples were calculated according to the methodology of Mills and Wang [26].

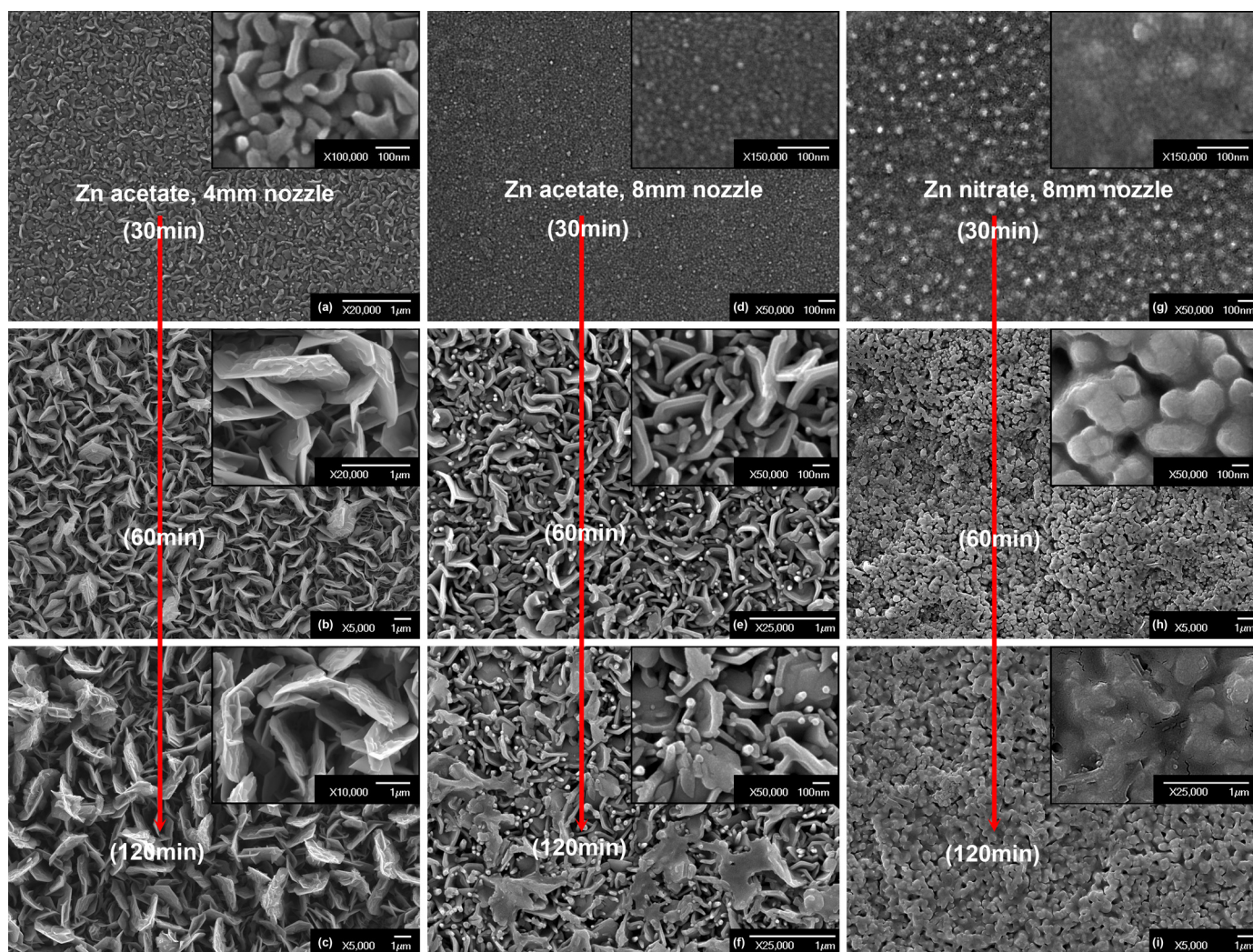


Fig. 2. SEM images of ZnO samples deposited by USP for 30, 60 and 120 min on Corning glass substrates, using a Zn acetate precursor solution and a 4 mm nozzle (a–c) or an 8 mm nozzle (d–f), and a Zn nitrate precursor and an 8 mm nozzle (g–i).

3. Results and discussion

Prior to deposition, the spraying conditions (such as nozzle diameter, distance between nozzle and substrate and substrate temperature) were optimized so that compact samples covering uniformly the substrate could be obtained. It was observed that

deposition times longer than 30 min are required in order to produce samples with good adhesion (passing the Scotch tape test) and long term stability (having similar properties after approximately six months).

Fig. 1 depicts typical X-ray diffraction patterns of pure ZnO samples deposited by the USP technique at 400 °C after 30, 60 and 120 min, using a 0.5 M zinc acetate precursor solution and a 4 mm diameter nozzle at a 5 cm distance between nozzle and substrate. The thickness of the 30, 60 and 120 min ZnO samples is ~50 nm, ~1375 nm and ~2250 nm, respectively. On the other hand, the corresponding thickness for 30, 60 and 120 min of deposition, using an 8 mm diameter nozzle (keeping the distance between nozzle and substrate at 5 cm) is ~30 nm, ~700 nm and ~1000 nm, respectively. All the diffraction peaks observed for the ZnO samples are in good agreement with the JCPDS card (No. 36-1451) for a typical hexagonal wurtzite type crystal, while no other characteristic peaks corresponding to possible impurities, such as zinc nitrate or zinc hydroxide, could be observed in the XRD patterns.

It is worth noticing that once a 4 mm nozzle is used, the increase of deposition time from 30 up to 120 min drastically changes the crystal properties of the ZnO samples [16], as shown in the corresponding XRD patterns [see Fig. 1(a)–(c)]; for 30 min the as-grown ZnO samples show a clear (002) preferential orientation

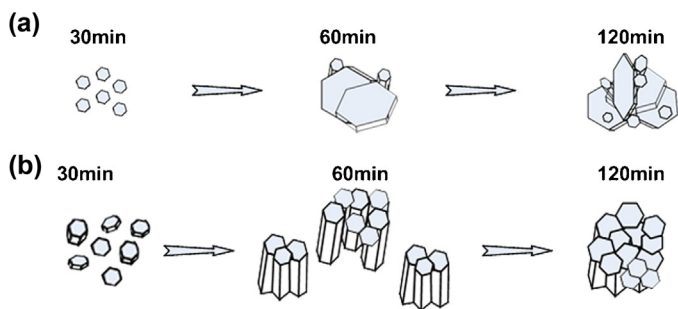


Fig. 3. ZnO growth mechanism using the USP technique with an 8 mm nozzle at 400 °C for a 0.5 M Zn acetate (a) and a 0.5 M Zn nitrate (b) precursor solution, respectively.

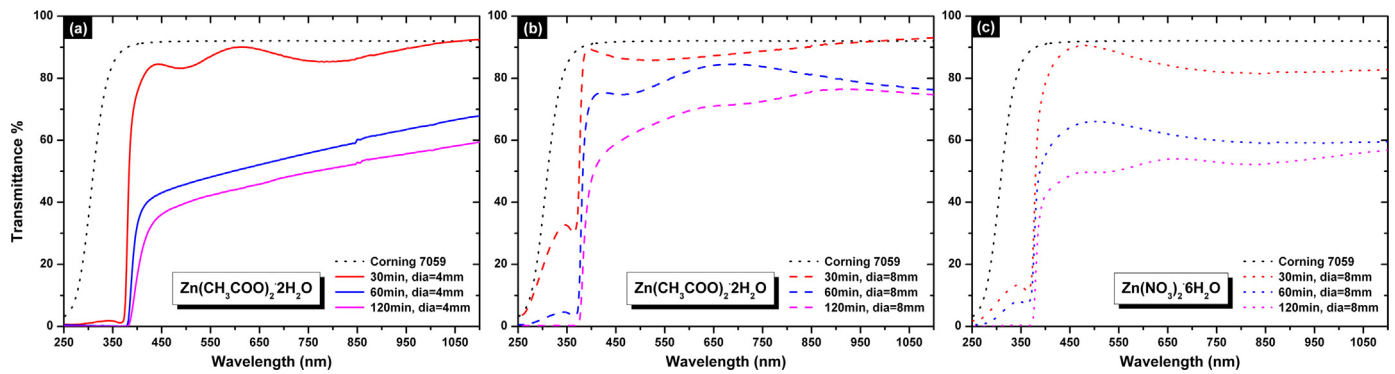


Fig. 4. Optical transmittance spectra of ZnO samples deposited at 400 °C by USP for 30, 60 and 120 min on Corning glass substrates, using a 0.5 M Zn acetate precursor solution and a 4 mm nozzle (a) or an 8 mm nozzle (b), and a 0.5 M Zn nitrate precursor and an 8 mm nozzle (c).

Table 1

Thickness (nm) of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y = 0.00, 0.01, 0.03, 0.05$) samples, deposited at 400 °C on Corning glass substrates, using the USP technique with an 8 mm-diameter nozzle.

Deposition time (min)	Al concentration			
	0%	1%	3%	5%
30	30 nm	45 nm	60 nm	65 nm
60	1375 nm	2500 nm	2500 nm	2720 nm
120	2250 nm	4100 nm	4230 nm	4400 nm

along the *c*-axis, i.e., perpendicular to the substrate applied [see Fig. 1(a)], while for longer deposition periods (up to 120 min) the XRD patterns reveal all the diffraction peaks related with the hexagonal wurtzite structure [see Fig. 1(b)–(c)].

On the other hand, when an 8 mm diameter nozzle is used, regardless the nature of the precursor solution (0.5 M zinc acetate or zinc nitrate solutions) the X-ray diffraction patterns of the ZnO samples deposited by the USP technique after 30, 60 and 120 min (not shown here) always exhibit the (0 0 2) plane, indicating the tendency of preferential crystallite growth vertically to the surface (*c*-axis oriented), in agreement with other research groups [15]. Moreover, the thickness of the as-grown ZnO samples was measured to be ~45 nm, ~1020 nm and ~1550 nm for a deposition

period of 30, 60 and 120 min respectively, using an 8 mm nozzle and the Zn nitrate precursor. To understand the growth mechanism of the ZnO films obtained with the two different Zn precursors, one should take into account the thickness of the samples along with the XRD results. As it was found out, the growth rate of the ZnO samples deposited after 30 min using Zn acetate as a precursor was 1 nm/min, while, in the case of Zn nitrate it was 1.5 nm/min. The larger growth rate observed for the Zn nitrate precursor is also supported by XRD, since the ZnO samples produced exhibit stronger (0 0 2) diffraction peaks, indicating that the (0 0 2) preferential growth orientation is favored when the Zn nitrate precursor is used [15]. These observations clearly indicate a difference in the crystal growth rate depending on the nature of the precursor solution [27].

Fig. 2(a)–(i) illustrate SEM images of the ZnO samples deposited by USP for 30, 60 and 120 min on Corning glass substrates using either Zn acetate [Fig. 2(a)–(f)] or Zn nitrate precursor [Fig. 2(g)–(i)], for 4 mm [Fig. 2(a)–(c)] and 8 mm nozzle diameter [Fig. 2(d)–(i)]. Thus, for the case of Zn acetate precursor and 4 mm nozzle diameter, at 30 min growth time, ZnO nanopetals occur, having a thickness of ~25 nm and a length of ~100–150 nm [see the inset of Fig. 2(a)]. Some nanowires of ~20 nm diameter, emerging perpendicular to the substrate, can be also observed. For

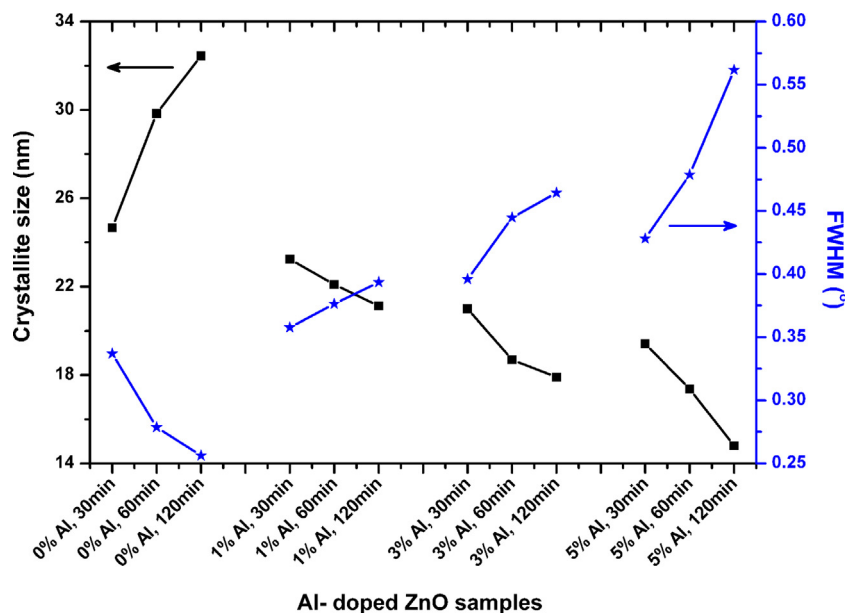


Fig. 5. Crystallite size as calculated using Scherrer's equation for $2\theta = 34.40^\circ$ (black curves with squares), along with the FWHM of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y = 0.00, 0.01, 0.03, 0.05$) samples (blue curves with stars), as a function of % Al molar concentration and deposition time.

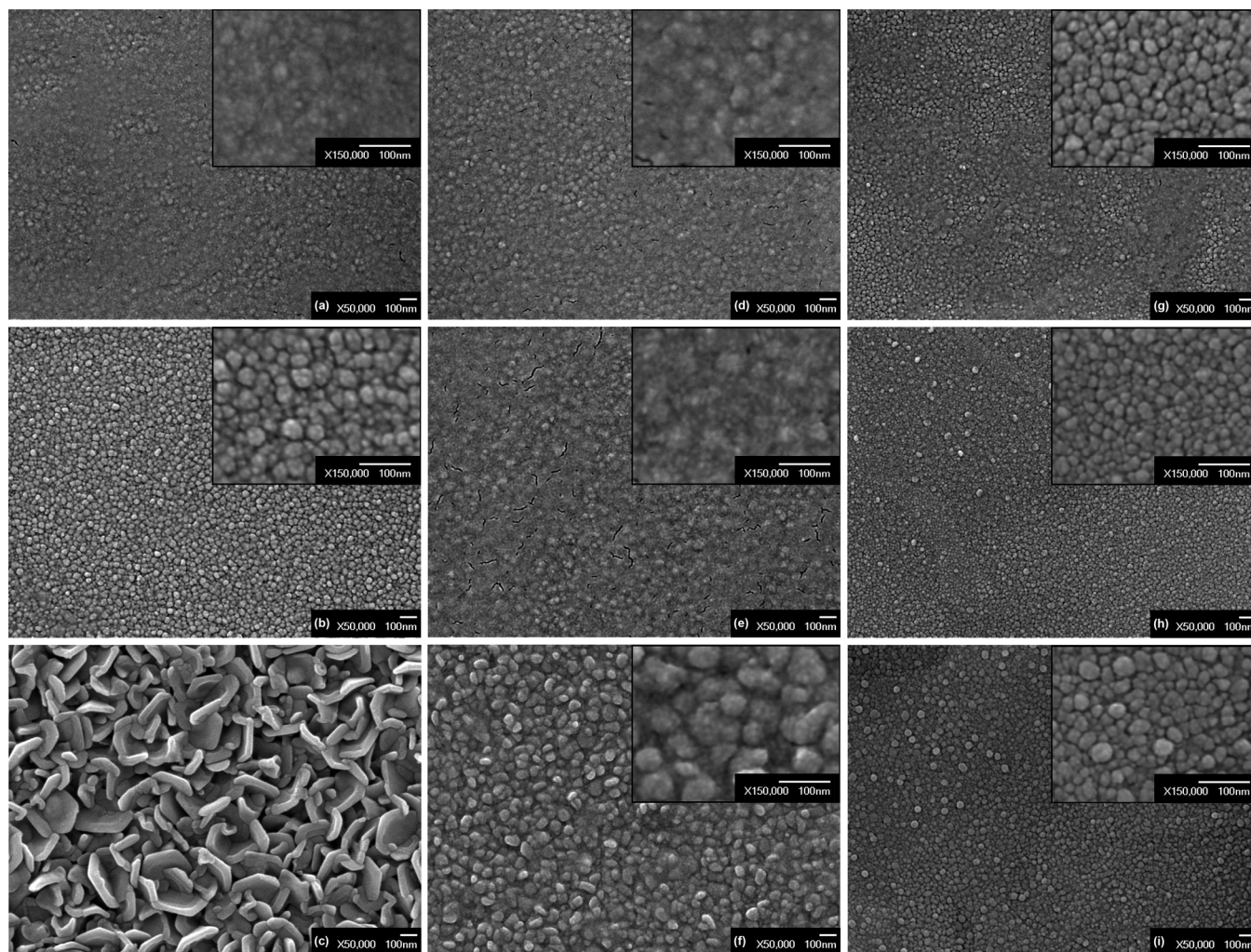


Fig. 6. SEM images of Al-doped ZnO samples deposited at 400 °C by USP for 1% Al (a: 30 min, b: 30 min, c: 30 min deposition), 3% Al (d: 30 min, e: 30 min, f: 30 min deposition), and 5% Al (g: 30 min, h: 30 min, i: 30 min deposition), respectively. A 0.5 M zinc acetate precursor solution and an 8 mm diameter nozzle were used.

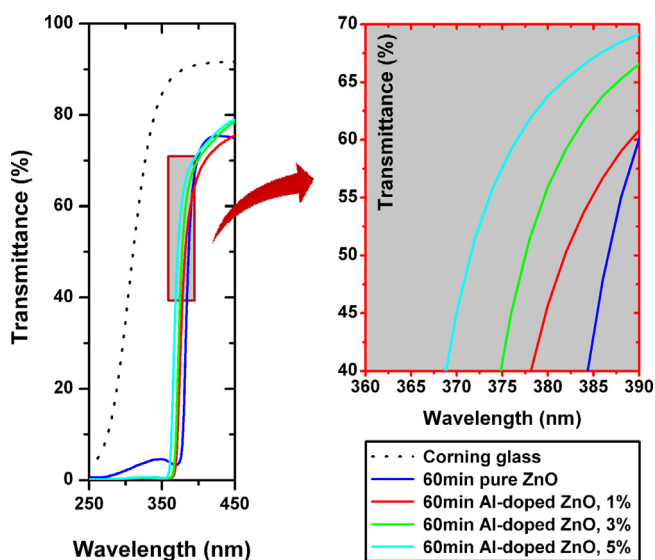


Fig. 7. Optical transmittance spectra of the $\text{Al}_x\text{Zn}_{1-y}\text{O}$ ($y = 0.00, 0.01, 0.03, \text{ and } 0.05$) samples deposited by the USP technique at 400 °C for 60 min. In the inset of Fig. 7 one can notice the blue shift of the transmission spectrum with increasing % Al molar concentration.

60 min spraying time, the nanopetals grow substantially reaching a length of $\sim 1\text{--}2\ \mu\text{m}$, while their thickness remains almost unaffected [see the inset of Fig. 2(b)]. Finally, for Zn acetate precursor and 4 mm nozzle diameter, at 120 min spraying time, the length of the reported nanopetals reaches $\sim 2\text{--}3\ \mu\text{m}$.

Fig. 3 depicts the suggested ZnO growth mechanism using the USP technique at 400 °C with an 8 mm-diameter nozzle for a 0.5 M Zn acetate [Fig. 3(d)] or Zn nitrate [Fig. 3(g)] precursor solution. As seen from Fig. 2(d)–(g) and Fig. 3, the ZnO samples for 30 min are quite smooth granular films, not though really homogeneous, consisting of grains with a diameter of about 20 and 50 nm for the Zn acetate and the Zn nitrate precursor solutions, respectively. The respective RMS roughness was estimated using AFM to be around 2–2.5 and 4–5 nm, values indicating quite low roughness.

With increasing deposition time (60 min), the samples grown using the Zn acetate precursor solution and an 8 mm-diameter nozzle [Fig. 2(e)] appeared to become highly nanostructured due to the coexistence of nanorods (with a diameter in the range of $\sim 20\text{--}30\ \text{nm}$) and hexagonal nanopetals (with a length of around $\sim 400\text{--}450\ \text{nm}$ and a thickness of $\sim 20\text{--}30\ \text{nm}$), both grown perpendicular to the surface. Moreover, the samples exhibited much higher RMS roughness, namely 45–50 nm. On the other hand, again for an 8 mm-diameter nozzle, the use of the Zn nitrate precursor solution gives rise to ZnO nanorods with a diameter of $\sim 100\text{--}150\ \text{nm}$, which were observed to agglomerate giving a quite dense surface [Fig. 2(h)].

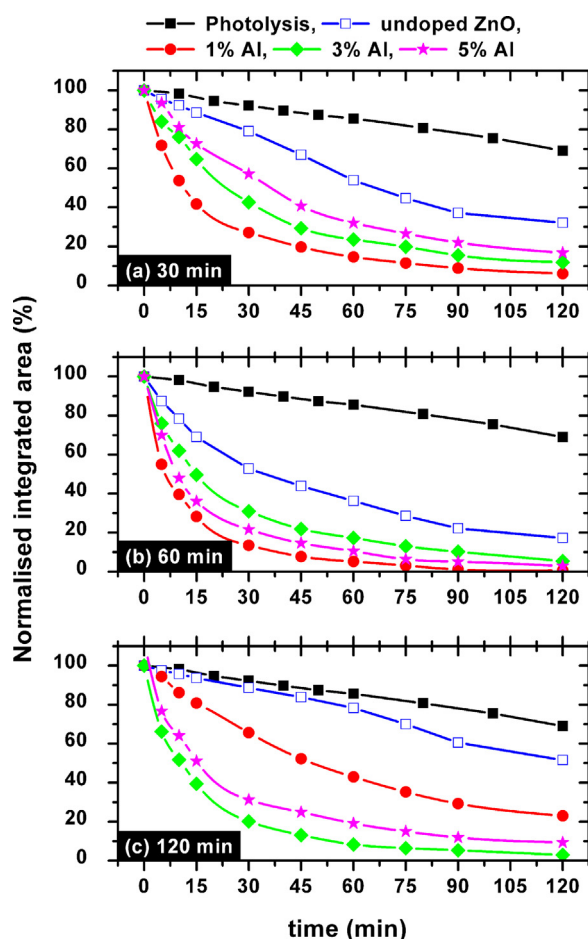


Fig. 8. Normalized integrated area vs. irradiation time for the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y=0.00, 0.01, 0.03, \text{ and } 0.05$) samples deposited by the USP technique at 400°C for 30 min (a), 60 min (b) and 120 min (c), respectively. For comparison reasons, the photolysis curve (black solid squares) is also presented.

For even longer deposition periods (120 min), the Zn acetate precursor produces samples consisting mainly of flat plates with nanorods standing between them [see Fig. 2(f)], while the Zn nitrate precursor gives even denser ZnO nanorods [see Fig. 2(i)] with a diameter of $\sim 100\text{--}150\text{ nm}$ and almost no empty space between them.

The optical transmittance spectra of the ZnO nanostructured thin films in the wavelength region $250\text{--}1100\text{ nm}$ are presented in Fig. 4. For both precursor types and nozzle diameters, at 30 min, all ZnO samples are highly transparent in the visible wavelength region, showing an average transmittance of about $85\text{--}90\%$, while a fall-off for wavelengths shorter than 380 nm occurs, characteristics of good quality ZnO coatings. Moreover, an additional absorption band centered near 365 nm was clearly recorded mainly for 30 and 60 min, band that can be attributed to excitonic resonances [17]. Finally, one can notice from Fig. 4(a) and (b) that ZnO samples grown for 60 and 120 min on Corning glass substrates using the Zn

acetate precursor and a 4 mm-diameter nozzle are less transparent than the ones produced with an 8 mm-diameter nozzle (reaching not quite 35% at 400 nm for a deposition period of 120 min), due to their increased thickness.

For the Al-doped ZnO samples deposited at 400°C for 30–120 min using an 8 mm-diameter nozzle, nanostructured thin films were produced, their thickness increasing with Al doping, as shown in Table 1. Furthermore, Al-doping was found to improve the crystallinity of the spray-deposited samples, which were dominated by the (002) plane of the ZnO wurtzite structure, a behavior implying preferential orientation of the crystallites perpendicular to the substrate surface. A comparison of the XRD patterns of the Al-doped ZnO thin films (not shown here) with those of the pure ZnO thin films, reveals a considerable increase in the wurtzite (002) diffraction peak intensities for the Al-doped samples, a behavior that can be attributed to an enhancement of the crystallinity because of the substitution reaction between Zn and Al [28]. Indeed, the difference in the atomic radii between Zn and the dopant Al atoms can probably lead to interstitial reactions, which may result in more intense wurtzite (002) diffraction peaks in the XRD patterns as well as higher growth rates [28]. The increase of the growth rate for the Al-doped ZnO samples was clearly indicated by their thickness, which was found to be almost double than that of the pure ZnO samples. The intensity of the (002) diffraction peak was observed to be almost unaffected by the % nominal Al concentration, while the crystallite size was found to decrease, approaching 15 nm for 5% Al concentration (see Fig. 5). Using the (002) peak broadening (Full Width at Half Maximum value) from the XRD pattern and the Scherer's formula, the crystallite size (d) was determined for the Al-doped ZnO samples, as presented in Fig. 5. It is obvious from Fig. 5 that Al doping leads to much smaller crystallite size values compared to pure ZnO, something that will strongly affect the photocatalytic activity of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y=0.01, 0.03, 0.05$) samples (vide infra). At the same time the crystallite size reduces gradually with increasing Al doping. This phenomenon is attributed to the nucleation mechanism of the ZnO phase, since, generally, an increase of Al concentration will enhance the nucleation of the ZnO phase and consequently result in smaller crystallite size [28].

Fig. 6(a)–(i) depict SEM images of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y=0.01, 0.03, 0.05$) samples deposited by USP for 30, 60 and 120 min on Corning glass substrates using an 8 mm-diameter nozzle at 400°C . As seen in Fig. 6(a), for 1% Al-doping and 30 min spraying period, homogeneous thin films were derived with a grain size of $\sim 25\text{ nm}$. For 60 min deposition time [see Fig. 6(b)], the 1% Al-doped ZnO thin films become denser with a grain size of $\sim 20\text{--}40\text{ nm}$, while for 120 min nanopetals occur, having a thickness of $\sim 30\text{--}40\text{ nm}$ and a length of $\sim 200\text{--}250\text{ nm}$ [see Fig. 6(c)]. As seen in Fig. 6(d) and (e), for 30 and 60 min deposition time and 3% Al concentration, more compact films were produced, while for 120 min, ununiformed grain-like films can be observed with a grain size of $\sim 50\text{--}100\text{ nm}$ [see Fig. 6(f)]. Increasing Al doping concentration to 5% was found to result in more compact films with better shaped grains [see Fig. 6(g)–(i)]. The reason is that the continuous spraying procedure (from 30 up to 120 min) allows the Al atoms to relocate at positions with lower free energy and to grow laterally [28]. Consequently, the Al-doped ZnO thin films become denser.

All the Al-doped ZnO samples are highly transparent in the visible regime, while the UV absorption edge of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y=0, 0.01, 0.03, 0.05$) samples is blue-shifted with increasing % Al doping concentration, indicating a broadening of the optical band gap [29–30] (see for example the case of 60 min deposition time and 0, 1, 3 and 5 % nominal Al concentration in Fig. 7). By doping with Al, the aluminum atoms occupy the zinc sites in the ZnO lattice. Thus, at room temperature they act as singly ionized donors

Table 2
Photocatalytic activity of $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y=0.00, 0.01, 0.03, 0.05$) samples regarding the degradation of stearic acid at 30 min exposure under UV-A illumination.

Deposition time (min)	Al concentration			
	0%	1%	3%	5%
30	20.95	72.89	57.33	42.86
60	47.25	86.50	69.06	78.42
120	11.39	34.40	79.88	68.84

giving one extra electron. These donor electrons occupy the states at the bottom of the conduction band, and therefore, as doping concentration is increased, these states get filled with donor electrons, which results in widening of a band gap and blue-shift of the transmission spectra (Burstein–Moss effect) [31,32].

Fig. 8 presents the normalized integrated area vs. irradiation time curves for pure and Al-doped ZnO samples deposited by USP on Corning glass substrates for 30–120 min spraying time at 400 °C. For comparison reasons, the photolysis curve (no catalyst present) is also displayed in Fig. 8. It can be readily observed that all the Al-doped samples show significantly better photocatalytic activity regarding the degradation of stearic acid than the pure ZnO ones, since, most probably, as already mentioned, they show better crystallinity and much smaller grain size. Table 2 summarizes the photocatalytic activity of the $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y = 0.00, 0.01, 0.03, 0.05$) samples at 30 min exposure under UV-A light illumination.

Thus, the most photocatalytically active sample with 1% nominal Al-doping is that for 60 min deposition time (degrading SA by ~86.5 % at 30 min), since it consists of well-shaped grains with a diameter of 20–40 nm, while the sample with the smallest photocatalytic performance is the one at 120 min, which comprises of nanopetals with relatively larger dimensions (wall thickness of 30–40 nm, diameter of 200–250 nm).

Similarly, among the 3% Al-doped samples, we observe that the sample deposited at 60 min is more efficient than that produced at 30 min, since it consists of denser and more uniform grains with a diameter of ~20–40 nm; it therefore exhibits larger effective surface area. However, for 120 min spraying period, the as-grown sample shows the highest photocatalytic activity (degrading SA by ~80% at 30 min), since it consists of nanopetals with just ~10 nm thickness and a diameter of ~50–100 nm [see Fig. 6(f)], thus leading to the maximum surface area and photocatalytic efficiency amongst the 3% Al-doped samples.

The photocatalytic activity for the Al-ZnO samples with 5% nominal Al concentration is similar with the 1% Al-doped ones; the sample deposited at 60 min is more efficient than that at 30 min, since it consists of smaller and more uniform grains with a diameter of ~15–25 nm. For 120 min deposition time, the sample seems more compact with larger grains (~20–40 nm), thus having smaller surface area and lower photocatalytic performance.

Following the methodology explained by Mills and Wang [26] and Paz et al. [33] each cm^{-1} of normalized integrated area as presented in Fig. 8 corresponds to 9.7×10^{15} molecules of stearic acid [or $(9.7 \times 10^{15})/(6.023 \times 10^{23})$ moles of SA]. As already reported, the UV-A light source used in our photocatalytic activity tests was an HPK 125 W Philips mercury lamp with an incident light intensity of 8.9 mW/cm^2 (or 9.471×10^{16} photons/sec). Thus, the SA disappearance rate (mol/min) and the formal quantum efficiency (FQE) at 30 min exposure under UV-A illumination were calculated for the pure and Al-doped ZnO samples. The pure ZnO samples grown by USP for 60 min at 400 °C using a 4 mm-diameter nozzle exhibit an FQE value of 0.06×10^{-3} and a SA disappearance rate of $\sim 5.65 \times 10^{-10}$ mol/min at 30 min, while the corresponding FQE and disappearance rate values in the case of an 8 mm-diameter nozzle are 1.06×10^{-3} and $\sim 9.99 \times 10^{-9}$ mol/min, respectively. This finding is expected since, if we look at the SEM images for the 4 and 8 mm-diameter nozzles [Fig. 2(b)–(e), respectively], we will notice that the samples grown by the USP technique using an 8 mm-diameter nozzle are characterized by smaller nanostructures, thus leading to higher effective surface area. Finally, the 5% Al-doped sample, deposited at 60 min, shows significantly better photocatalytic activity at 30 min (FQE = 3.07×10^{-3} and SA disappearance rate = 2.90×10^{-8} mol/min), since it is the most uniform thin film with the smallest grain size, i.e., ~15–25 nm [see Fig. 6(h)]. At this point, it should be noted that the photocatalytic activity of all $\text{Al}_y\text{Zn}_{1-y}\text{O}$ ($y = 0.00, 0.01, 0.03, 0.05$) samples regarding the

% decomposition of SA is always significantly higher than that observed due to photolysis, i.e., light irradiation of SA in the absence of a metal oxide catalyst. At 30 min, for example, the % SA degradation due to photolysis is ~8%, reaching an FQE value of only 0.05×10^{-3} and a SA disappearance rate of $\sim 4.44 \times 10^{-10}$ mol/min.

4. Conclusions

ZnO and Al-ZnO nanostructured thin films were deposited on Corning glass substrates by ultrasonic spray pyrolysis, a simple, environmental-friendly and inexpensive method, using aqueous precursor solutions at 400 °C. We have thoroughly studied the influence of precursor type, deposition time and doping concentration on the morphological, optical, and photocatalytic properties of the pure and Al-doped ZnO samples. All samples show very good crystallinity, while their texture and morphology depend strongly on the deposition parameters, such as precursor solution, growth time and nozzle diameter. The as-grown samples are either homogenous thin films, which become denser with Al-doping, or consist of nanopetals whose dimensions increase drastically with spraying time. All Al-ZnO samples show very good photocatalytic activity regarding the degradation of stearic acid, a behaviour which is mainly attributed to their good crystallinity and large effective surface area. In particular, the Al-doped samples show significantly better photocatalytic activity than the pure ZnO ones, since they exhibit increased crystallinity and much smaller grain size.

Acknowledgements

This project is implemented through the Operational Program “Education and Lifelong Learning”, Action Archimedes III and is co-financed by the European Union (European Social Fund) and Greek national funds (National Strategic Reference Framework 2007–2013).

References

- [1] A. Mills, S. Lee, J. Photochem. Photobiol. A 152 (2002) 233–247.
- [2] I.M. Arabatzis, S. Antonaraki, T. Stergiopoulos, A. Hiskia, E. Papaconstantinou, M.C. Bernard, P. Falaras, J. Photochem. Photobiol. A 149 (2002) 23–245.
- [3] S.B. Kim, S.C. Hong, Appl. Catal. B: Environ. 35 (2002) 305–315.
- [4] Y.H. Hsien, C.F. Chang, Y.H. Chen, S.F. Chang, Appl. Catal. B: Environ. 31 (2001) 241–249.
- [5] M. Rosana, W. Alberici, F. Jardim, Appl. Catal. B: Environ. 14 (1997) 55–68.
- [6] L. Xiao-e, A.N.M. Green, S.A. Haque, A. Mills, J.R. Durrant, J. Photochem. Photobiol. A 162 (2004) 253–259.
- [7] K. Guan, Surf. Coat. Technol. 191 (2005) 155–160.
- [8] G. Kenanakis, E. Stratakis, K. Vlachou, D. Vernardou, E. Koudoumas, N. Katsarakis, Appl. Surf. Sci. 254 (2008) 5695–5699.
- [9] S.H. Lee, S. Pumprueg, B. Moudgil, W. Sigmund, Colloid Surf. B 40 (2005) 93–98.
- [10] K.M. Parida, S.S. Dash, D.P. Das, J. Colloid Interface Sci. 298 (2006) 787–793.
- [11] M. Suzuki, T. Ito, Y. Taga, Appl. Phys. Lett. 78 (2001) 3968–3970.
- [12] P.V. Kamat, R. Huehn, R. Nicolaescu, J. Phys. Chem. B 106 (2002) 788–794.
- [13] P. Singh, A. Kumar, D. Deepak, Kaur, J. Cryst. Growth 306 (2007) 303–310.
- [14] D. Perednis, L.J. Gauckler, J. Electroceram. 14 (2005) 103–111.
- [15] E. Bacaksiz, M. Parlak, M. Tomakin, A. Özçelik, M. Karakiz, M. Altunbaş, J. Alloys Compd. 466 (2008) 447–450.
- [16] G. Kenanakis, Z. Giannakoudakis, D. Vernardou, C. Savvakis, N. Katsarakis, Catal. Today 151 (2010) 34–38.
- [17] R.J. Lang, J. Acoust. Soc. Am. 43 (1962) 6–8.
- [18] D. Vernardou, E. Stratakis, G. Kenanakis, H.M. Yates, S. Couris, M.E. Pemble, E. Koudoumas, N. Katsarakis, J. Photochem. Photobiol. A 202 (2009) 81–85.
- [19] A. Mills, S. Lee, A. Lepre, I.P. Parkin, S.A. O'Neill, Photochem. Photobiol. Sci. 1 (11) (2002) 865–868.
- [20] A. Mills, J. Wang, Photochem. Photobiol. A 182 (2006) 181–186.
- [21] T. Sawunuma, L. Jiang, A. Fujishima, K. Hashimoto, J. Phys. Chem. B 101 (1997) 11000–11003.
- [22] M.E. Simonsen, H. Jensen, Z. Li, E.G. Søgaard, Photochem. Photobiol. A 200 (2008) 192–200.
- [23] D. Vernardou, G. Kalogerakis, E. Stratakis, G. Kenanakis, E. Koudoumas, N. Katsarakis, Solid State Sci. 11 (2009) 1499–1502.
- [24] J. Shang, W. Li, Y. Zhu, J. Mol. Catal. A: Chem. 202 (2003) 187–195.

- [25] A. Mills, N. Elliott, I.P. Parkin, S.A. O'Neill, R.J. Clark, J. Photochem. Photobiol. A: Chem. 151 (2002) 171–179.
- [26] A. Mills, J. Wang, Photochem. Photobiol. A 182 (2006) 181–186.
- [27] L. Znaidi, G.J.A.A. Soler Illia, S. Benyahia, C. Sanchez, A.V. Kanaev, Thin Solid Films 428 (2003) 257–262.
- [28] K. Lin, P. Tsai, Thin Solid Films 515 (2007) 8601–8604.
- [29] Wang K.E. Lee, S.H. Hahn, E.J. Kim, S. Kim, J.S. Chung, Eu W. Shin, C. Park, Mater. Lett. 61 (2007) 1118–1121.
- [30] T. Ratana, P. Amornpitoksuk, T. Ratana, S. Suwanboon, J. Alloys Compd. 470 (2009) 408–412.
- [31] B.E. Sernelius, K.F. Berggren, Z.C. Jin, I. Hamberg, C.G. Granqvist, Phys. Rev. B 37 (17) (1988) 10244–10248.
- [32] B. Joseph, P.K. Manoj, V.K. Vaidyah, Ceram. Int. 32 (2006) 487–493.
- [33] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, J. Mater. Res. 10 (1995) 2842–2848.