# 1D Nanostructured ZnO Layers by Microwave - Assisted Hydrothermal Synthesis

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ZnO 1D nanostructures have been gaining more and more advanced applications in various fields from electronics and optoelectronics to environment protection and medicine due to the synergy between the unique properties of semiconductor zinc oxide and those of 1D nanostructures. This paper investigates the microwave (MW)-assisted hydrothermal synthesis of 1D nanostructured ZnO layers grown on glass substrates to be used in optoelectronic applications. The effects of MW-irradiation power (400-600 W) and span (3-6 min) on the morphology, microstructure and optical properties (transmittance, reflectance, absorption coefficient and refractive index) of the resulted nanostructured layers were investigated by SEM, FTIR and UV-Vis-NIR spectroscopy. The band gap energy was calculated from optical absorbance spectra in UV-Vis range. The obtained ZnO nanostructured layers show optical transmittance between 58 and 87% and low reflection between 4.2-6.8 % at normal incidence of light in the visible spectra and transmittance values from 75 to 85% and reflectance between 4.8 and 6.7% in the near infrared spectra.

Keywords: microwave-assisted hydrothermal synthesis, 1D nanostructured layer, ZnO, morphology and crystallinity, optical properties

ZnO 1D nanostructures have been gaining more and more advanced applications in various fields from electronics and optoelectronics to environment protection and medicine due to the synergy between the unique properties of zinc oxide semiconductor and those of 1D nanostructures. Zinc oxide (ZnO) is the most important wide band gap (3 eV) n-type semiconductor with thermal and chemical stability at room temperature used in large scale optoelectronic applications due to its unique optical and electrical properties [1-2] with an extended excitation binding energy of 60 meV [2-3]. When zinc oxide is obtained in nanostructured form with different morphologies such as nanorods, nanowires, nanoflowers, quantum dots, nanopetals [2, 4-5], it acquires new chemical, luminescent and optoelectronic properties due to increased surface to volume ratio and to their quantum confinement effect [2, 6-7, 8].

Zinc oxide nanomaterials can be obtained on glass substrate as well as on flexible and polymers smooth substrates by chemical and physical methods such as solgel, CVD, MOCVD, hydrothermal synthesis and thermal evaporation method [5, 9]. In recent years, the hydrothermal method is one of the most used for synthesizing metal oxides nanostructures [6-7, 10-12] because it provides good control over homogeneity, particle size, chemical composition, phase and morphology of the obtained products. The microwave-assisted hydrothermal synthesis of nanostructured materials has attracted attention by simplicity and efficiency, as well as the possibility of large-scale production of high quality nanostructures [13-14]. The major advantage of this method is the ability to enhance the reaction temperature increasing the reaction rate by 10 to 1000 times, thereby reactions can be completed within minute or even seconds [14-15]. The molecules subjected to microwave irradiation at frequency of 2.45 GHz, at which all domestic microwave ovens and commercial microwave reactors for chemical synthesis operate, vibrate at  $4.9 \times 10^9$  times per second by aligning and realigning with the oscillating field and thus creating a large internal heat that can climb very fast even at 100 °C per second [14, 16]. These result in reaction time, homogeneous volumetric heating, low energy consumption and therefore low manufacturing cost [2, 6, 17]. Soleimanzadeh et al have grown zinc oxide nanostructures on different substrates using a sequential hydrothermal assisted microwave method and obtained nanorods with a growth rate of 4.2 µm/min [7].

Recent studies demonstrated that microwave irradiation does not change the crystalline structure of zinc oxide but can modify the electronic structure of the band gap by creating vacancy defects that originated from the rapid synthesis process, improving the electronic properties for applications in optoelectronic devices and enhancing their catalytic activity [15-16]. The effects of working parameters (MW power, MW irradiation time) during microwave-assisted synthesis of 1D ZnO nanostructures with an aspect ratio (ÅR) of 10 or higher were investigated by Zhu et al [10]. Shojaee and his coworkers highlighted the important role of the precursor concentration on the size of obtained nanostructures; increasing the concentration from 0.001 to 0.1 M leads to a decrease in the average diameter of the nanostructures from 136 to 117 nm [6]. Increasing irradiation power also can diminish the diameter of nanostructures but can increase the density of nanostructures on the substrate surface. Also with the increase in irradiation time from 2 to 3 minutes, a slight decrease in the average diameter of the nanorods was observed, but the most important effect was on the morphology of nanostructures (from nearly spherical to elongated) [6].

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This paper investigates the (MW)-assisted hydrothermal synthesis of 1D nanostructured ZnO layers grown on glass substrates to be used in optoelectronic applications. The effects of MW-irradiation power between 400-600 W and synthesis span between 3-6 min on the morphology, microstructure and optical properties (transmittance, reflectance, absorption coefficient and refractive index) of the resulted nanostructured materials were investigated by SEM, FTIR and UV-Vis-NIR spectroscopy. The band gap energy and absorption coefficient were calculated from optical absorbance spectra in UV-Vis range and the refractive index and extinction coefficient have been calculated from optical transmittance and reflectance spectra.

# **Experimental part**

#### Materials

All the reagents (analytical grade purity) were purchased from Sigma Aldrich and used as received, without any further purification.

## Growth of nanostructures

Zinc oxide nanostructures were synthesized on soda lima glass substrate by microwave-assisted hydrothermal method, varying the working wattage and time irradiation (table 1).

The nanostructured layers were grown into an equimolar aqueous solution of 0.025 M zinc nitrate hexahydrate  $(Zn(NO_{,})_{2}\cdot 6H_{,}O)$  and hexamethylenetetramine (HMTA,  $(CH_{,})_{6}N_{,4}^{2}$ ) using a sealed Teflon-lined autoclave and a domestic microwave oven. The substrates were submerged in the growth solution inside a Parr 4782 Microwave Digestion Vessel and the microwave irradiation was applied using a Samsung M71A Microwave oven. After removing from mother solution, the obtained samples were washed with warm and cold distilled water for several times and then with ethanol, drying in air and heated to 90 °C for 60 minutes.

#### Characterization of ZnO nanostructures

The morphology of the synthesized samples was characterized using Scanning Electron Microscope (SEM) FEI Quanta 200 with a conventional tungsten electron source giving a resolution of 3.5 nm and ultra-high Field Emission Scanning Electron Microscope (FEG-SEM)-Nova NanoSEM 630.

The crystalline structure of nanostructures was identified by X-ray diffractometry using a Rigaku SmartLab X-ray diffractometer (Cu radiation).

The Fourier transform infrared (FTIR) absorption spectra were recorded in range of 400-4000 cm<sup>-1</sup> using ALPHA FT-IR Bruker Spectrometer with Eco-ATR single reflection ATR module (equipped with a ZnSe ATR-crystal), on powder samples detached from the substrates they grew up.

The optical transmission and reflectance spectra of the layers were acquired at room temperature with a Perkin Elmer Lambda 35 spectrometer, operated in air, at normal incidence, in the 200-1100 nm spectral range. The band gap energy and absorption coefficient were calculated from optical absorbance spectra in UV-VIS range [18] and the refractive index and extinction coefficient have been calculated from optical transmittance and reflectance spectra [19].

### **Results and discussions**

Effect of MW-irradiation power

Figure 1 shows top-view SEM images of ZnO-based nanostructures obtained during irradiation for three minutes with different MW power values

The morphological modifications obtained from SEM analysis data consist of decreasing average diameter from 46 to 29 nm and increasing average length from 124 to 170 nm, respectively, resulting in an increase of the aspect ratio (AR) of 1D nanostructures (nanorods) from 2.68 to 5.86 (table 1).

Table 1							
INVESTIGATED SAMPLES OBTAINED BY THE MV-ASSISTED HYDROTHERMAL METHOD AND THEIR MORPHO-STRUCTURAL AND							
OPTOELECTRONIC PROPERTIES							

Nr		Experimental parameters		Nanostructures parameters		Opto- electric properties
	Samples	MW Power (W)	MV irradiation span (min)	Nanostructures sizes (Diameter/Length) (nm) /AR, from SEM	Crystallite size(nm)/Interplanar distance(Å), rom XRD	Eg (eV)
1	S1	600	3	46/124 /2.69	11.7/2.837	3.768
2	S2	525	3	33/144 /4.36	23.0/2.827	3.664
3	S3	450	3	29/170 /5.86	23.8/2.812	3.592
4	S4	400	3	285/326 /1.14	23.1/2.819	3.700
5	<b>S</b> 5	400	4	310/606 /1.98	24.4/2.829	3.647
6	S6	400	6	203/520 /2.50	22.3/2.827	3.732



Fig.1. SEM images of ZnO nanostructures obtained at different MW-irradiation power values: 450 W (S1), 525 W (S2) and 600 W (S3)

All X-ray diffraction peaks of the obtained ZnO nanostructures (fig. 2) can be indexed to hexagonal wurtzite type ZnO structure with lattice constants, *a* and *c* ranging between 3.255-3.260 Å and 5.220-5.211 Å, respectively, consistent with the standard database (JCPDS file 36-1451).

The observation of the intensity evolution of the most important three diffraction peaks, located in 2 theta range of 30-40, of the obtained wurtzite type ZnO nanostructures shows a relatively higher increase in the intensity of (002) peak with the increase of MW-irradiation, which indicates a higher preferential growth along vertical c-axis. This onedimensional anisotropic growth of the nanostructures confirms the modification of the morphology of nanostructures having different growth rates in different directions of the crystal, towards the formation of 1D nanostructures (nanorods, nanwires) (fig. 1b). No peaks corresponding to impurities are detected, showing that the final products purely consist of ZnO.

The transmittance T(k) and reflectance R(k) spectra of the ZnO nanostructured layers obtained at different MWirradiation power, recorded between 200-1100 nm wavelength range at normal incidence, are illustrated in figure 3. All the samples show between 75 and 90% optical transmittance in the visible and near infrared range.

The obtained ZnO nanostructured layers show low reflection between 4.8-6.8% at normal incidence of light in both Vis and NIR spectra. Higher MW-irradiation power, lower reflectance value (S3 in fig. 3b). This can indicate an increase in the roughness of the nanostructured ZnO layer, because this behavior of reflectance decreasing with increasing MW-radiation power is similar to a broken glass which presents high roughness and low reflectance. The reduced reflectance for normal incidence is due to destructive interference of reflected light at the film/ substrate and air/film interfaces [20].



Fig. 2. XRD patters of ZnO nanostructured layers obtained at different MW-irradiation power values: 450 W (S1), 525 W (S2) and 600 W (S3)



Fig. 3. The transmittance (a) and reflectance (b) spectra of ZnO nanostructured layers grown at different MW-irradiation power values: 450 W (S1), 525 W (S2) and 600 W (S3)

The variation of the optical parameters (extinction coefficient, refractive index and band gap energy) of ZnO nanostructured layers is presented in figure 4. Figure 4a shows a significant variation of the extinction coefficient in the UV region (Detail A), which increases with the increase of the MW-irradiation power (from S1 to S3). Taking into account that k is directly proportional to the number/quantity of absorbent molecules/entities one can observe that increasing the irradiation power during MW-assisted synthesis leads to an increase in the AR of 1D nanostructured ZnO monocrystal entities (table 1).

Figure 4 b shows an almost linear decrease in refractive index (n) of the obtained nanostructured layers with increasing MW-irradiation. This behavior associated with the decrease in reflectance (fig. 3b) could be explained by *Moth Eye* 'effect. Because the nanostructure's size and the distance between these nanostructures are subwavelength of visible light, the light behaves as if there is a continuous refractive index gradient between the air and the films surface. This led to a decrease in reflectance by effectively removing the air-material interface [20]. So, the obtained nanostructured layers with size in the range of subwavelength of visible light can act as anti-reflective coating.

The optical absorption edge of the obtained nanostructured layers (detail A in fig. 4c) shows a redshift to the region of lower photon energy, when MW-irradiation power increases. According to quantum confinement effect [21], the increase in band gap energy values (red shift) of ZnO nanocrystalline films is associated to the increase of the crystallite size (table 1).



Fig. 4. The variation of extinction coefficient (a), refractive index (b) and áhí vs hí curves ( $E_g$  calculation) (c) of ZnO nanostructured layers grown at different MW-irradiation power values: 450 W (S1), 525 W (S2) and 600 W (S3)

# Effect of growth span

Figure 5 shows the SEM top-view images of ZnO nanostructures growth during 3-6 min under MW-irradiation at 400 W. One can observe an increase in both diameter and width, but also a small increase in AR when the



Fig. 5. SEM images of ZnO nanostructures obtained at different growth span: 3 min (S4), 4 min (S5) and 6 min (S6)

irradiation span rises from 3 min (S1) to 5min (S2). Thus, the diameter and length of the nanostructures grow from about 280 to 310 nm and 326 to 606 nm, respectively, and the A.R. increases from about 1.1 nm to about 2 nm, indicating morphological changes from 0D to 1D nanostructures. Increasing irradiation span to 6 min (S6) results in an increase of A.R. to 2.5 (table 1) associated with other morphological changes, as shown in figure 5. In a recent paper Sarwar Rana et al [22] who monitored the growth of ZnO nanostructures inside zinc acetate aqueous solution by MW-assisted methods, have found that the length and diameter of the ZnO nanorods increased until 5 min of irradiation, where their values saturate, due to the formation of ZnO nanostructures inside the solution (by homogeneous nucleation) rather than on the substrate (by heterogeneous nucleation). Even it is well known that the low interfacial energy at ZnO/substrate interface favors the hetero-geneous nucleation, at high temperatures under MW-irradiations in some solutions of reactants the homogeneous nucleation takes place inside the solution rather than on the substrate, resulting in growth stoppage of the nanostructure because no more reactants are available for the growth of nanostructures on a seeded substrate [22]. They have stated that for MW-irradiation hydrothermal method, 5 min duration is the transition time at which homogeneous nucleation supersedes heterogeneous nucleation [22].

As with the previous series of samples obtained with increasing MW-irradiation power between 450-600 W, in the case of samples with irradiation span between 3 - 6 min at 400 W, XRD diffraction patterns also show diffraction peaks that can be indexed to hexagonal wurtzite type ZnO structure (fig. 6), with lattice constants *a* and *c* ranging between 3.257-3.259 Å and 5.215-5.218 Å, respectively.

In this series (S4-S6), an increase in the intensity of all XRD peaks is also observed with increasing MW-irradiation span, indicating an increase in the quantity of wurtzite crystalline phase, but unlike the previous series (S1-S3 in



Fig. 6. XRD patters of ZnO nanostructured layers grown at different growth span: 3 min (S4), 4 min (S5) and 6 min (S6)





Fig. 7. The transmittance (a) and reflectance (b) spectra of ZnO nanostructured layers grown at different growth span: 3 min (S4), 4 min (S5) and 6 min (S6)

fig. 2), the increase in the irradiation span from 3 to 4 min shows only a slight increase of the relative intensity of (002) peak (S5), after which the intensity of this peak decreases in case of sample irradiated for 6 min (S6). This behavior confirms the morphological changes observed in SEM images (fig. 5) indicating a growth mechanism change within 4-6 min MW-irradiation span.

The transmittance T(k) and reflectance R(k) spectra of the ZnO nanostructured layers obtained at MW-irradiation span of 3-6 min at 400 W, recorded between 200-1100 nm wavelength range at normal incidence, are illustrated in figure 7. The spectra of the obtained layers show optical transmittance at normal incidence of light in the Vis and NIR range between 57- 82% and 72-85%, respectively, and reflectance between 4.8-6.7% in UV-Vis-NIR range.

For this series (S4-S6) no monotone variation of the optical parameter (extinction coefficient, refractive index and band gap energy) values with the increase of the MW-irradiation span was obtained, as can be observed

from figure 8. The variation of the optical parameters (extinction coefficient, refractive index and band gap energy) of ZnO nanostructured layers is shown in figure  $\hat{8}$ . Regarding the variation of the refractive index values (fig. 8b), a minimum at about 320 nm is observed for all samples, close variations of the values for the samples S 4 (3 min MW-irradiation) and S6 (6 min MW-irradiation) are highlighted, while for sample S5 (4 min MW-irradiation) the lowest values were obtained along the UV-Vis-NIR range. The same observation is also valid for the variation of the optical absorption edge of S4-S6 samples (Eg values and detail A in fig. 8c), that shows a redshift to the region of lower photon energy only when the MW-irradiation span increases from 3 (S4) to 5 (S5) min, after which a blue shift is observed when this increases to 6 min (S6). According to quantum confinement effect, these results are closely correlated with the crystallite size variation; smaller crystallite size higher Eg values (table 1).



Fig. 8. The variation of extinction coefficient (a), refractive index (b) and áhí vs hí curves (Eg calculation) (c) of ZnO nanostructured layers grown at different growth span: 3 min (S4), 4 min (S5) and 6 min (S6)



Fig. 9. FTIR spectra of ZnO nanostructures obtained by the microwave-assisted hydrothermal method

#### Molecular structure

Figure 9 shows the Fourier transform infrared (FTIR) spectra of the obtained nanostructured layers in the range between 2000 and 400 cm<sup>-1</sup>. One can observe the presence of a strong absorption peak at about 480cm<sup>-1</sup> and a lower intensity peak at 735 cm<sup>-1</sup> characteristic for Zn-O stretching modes [23], confirming the formation of zinc oxide phase for all the obtained samples.

The presence of weak absorption bands characteristic of functional groups C-H (at 1457 cm<sup>-1</sup>), N-H (at 1559cm<sup>-1</sup>) and COO (at 1419 and 1717 cm<sup>-1</sup>) in the FTIR spectra suggest a small impurification with reagents (HMTA and acetate) from the mother solution [23].

## Conclusions

ZnO nanostructured layers with wurtzite type pure phase were grown on glass substrates by MW-assisted hydrothermal method at 400-600 W irradiation power and 3-6 min span.

When MW-irradiation power increased from 450 to 600 W, for 3 min irradiation span, the increase in onedimensional anisotropic growth of the nanostructures with doubling the A.R. value from about 2.7 to 5.9 and Eg redshift to the region of lower photon energy were observed, due to the increase of crystallite size.

The obtained ZnŐ nanostructured layers show optical transmittance between 58 and 87% and low reflection between 4.2-6.8% at normal incidence of light in the visible spectra and transmittance values from 75 to 85% and reflectance between 4.8 and 6.7% in the near infrared spectra.

The decrease in refractive index of the obtained nanostructured layers associated with the decrease in reflectance when increasing MW-irradiation power results in nanostructures with size in the range of subwavelength of visible light that can act as anti-reflective coating.

A redshift of Eg values were observed for ZnO nanostructured layer when the MW-irradiation span increases from 3 to 5 min, followed by a blue shift when

the span value increases to 6 min, closely correlated with the crystallite size variation.

Acknowledgement. This work was supported by project PNII-No.27/2014-NANOZON.

# References

- 1. SHUJI, S., KAZUYA, M., J. Nano. Res., 10/2, 2008, p. 297.
- 2. JINGBIAO, C., Mater. Characteriz., **64**, 2012, p. 43.
- 3. ZL, W., J. Phy. Condens Mater, 16, 2004, p. R829.
- 4. OCAKOGLU, K., MANSOUR, SH.A., YILDIRIMCAN, S., AL-GHAMDI,
- A.A., EL-TANTAWY, F., YAKUPHANOGLU, F., 148, 2015, p. 362.

5. SARAHNAZ, S., GUJELA, O.P., AFZULPURKAR, N.V., Fabrication of Light Emitting Diode with ZnO Nanorods on Polymer Coated Silicon Substrate, 2013 International Conference on Manipulation, Manufacturing and Measurement on the Nanoscale (3M-NANO) 26-30 August 2013, Suzhou, China, 978-1-4799-1213-1/13/S31.00 ©2013 IEEE. 6. SHOJAEE, N., EBADZADEH, T., AGHAEI, A., **61**, 2010, p. 1418.

7. SOLEIMANZADEH, R., MOUSAVI, M.S.S., MEHRFAR, A., ESFAHANI, Z.K., KOLAHDOUZ, M., ZHANG, K., J. of Crystal Growth, **426**, 2015, p. 228

8. MUSAT, V., TABACARU, A., VASILE, B.S., SURDU, V.A., RSC Advances, 4/108, 2014, p. 63128.

9. SAMADI, M., ZIRAK, M., NASERI, A., KHORASHADIZADE, E., MOSHFEGH, A.Z., Thin Solid Films, **605**, 2016, p. 2.

10. ZHU, J.Y., ZHANG, J.X., ZHOU, H.F., QIN, W.Q., CHAI, L.Y., HU, Y.H., Trans. Nonferrous Met. Soc. China, **19**, 2009, p. 1578.

11. MUSAT, V., FORTUNATO, E., PURICA, M., MAZILU, M., BOTELHO DO REGO, A.M., DIACONU, B., BUSANI, T., Mater. Chem. and Phys., **132** (2-3), 2012, p. 339.

12. DANCIU, A.I., MUSAT, V., BUSANI, T., PINTO, J.V., BARROS, R., REGO, A.M., FERRARIA, A.M., CARVALHO, P.A., MARTINS, R., FORTUNATO, E., J. of nanoscience and nanotechnology, **13**(10), 2013, p. 6701.

13. ZIRAK, M., AKHAVAN, O., MORADLOU, O., NIEN, Y., MOSHFEGH, A.Z., J. Alloys Compd., **590**, 2014, p. 507.

14.MA, M.G., ZHU, Y.J., CHENG, G.F., HUANG, Y.H., Mater. Lett., **62**, 2008, p. 507–510.

15. BU, I.Y.Y., 39, 2013, p. 1189.

16. YOSHIDA, K., SONOBE, T., ZEN, H., HACHIYA, K., OKUMURA, K., MISHIMA, K., INUKAI, M., NEGM, H., TORGASIN, K., OMER, M., KINJO, R., KII, T., MASUDA, K., OHGAKI, H., J. of Phys. and Chem. of Solids, **83**, 2015, p. 47.

17. IVANOV, V.K., SHAPOREV, A.S., SHARIKOV, F.YU., BARANCHIKOV, A.YE., Superlattices and Microstruc., **42**, 2007, p. 421.

18. GHRAÏRI, N., AOUSGI, F., ZRIBI, M., KANZARI, M., Chalcogenide Lett., **7**(3), 2010, p. 217–225.

19. ILICAN, S., ZOR, M., CAGLAR, Y., CAGLAR, M., Optica Aplicata, **9**(1), 2006, p. 29–37.

20. M. MAZILU A, N. TIGAU A, B, V. MUSAT, Optical Mat, **34**, 2012, p.1833 21. PESIKA, N. S., HU, Z., STEBE, K. J., SEARSON, P. C., J. Phys. Chem. B, **106**, 2002, p. 6985.

22. SARWAR RANA, A. H., KANG, M. & KIM, H.-S., Scientific Reports, 6, 2016, Article DOI: 10.1038/srep24870,

23. GAYEN, R.N., SARKAR, K., HUSSAIN, S., BHAR, R., PALL, A.K., Indian J. pure and Appl. Phys, 49, 2011, p. 470.

Manuscript received: 4.03.2018