PREPARAREA ȘI CARACTERIZAREA AEROGELURILOR DE ZnO DISPERSATE ÎN MATRICE DE SILICE
ELABORATION AND CHARACTERIZATIONS OF ZnO AEROGEL NANOPARTICLES DISPERSED IN SILICA MATRIX

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Nanocomposite films formed by direct inclusion of ZnO aerogel nanoparticles in liquid state silica matrix and deposited by dip and spin-coating techniques on glass substrates were elaborated. The ZnO aerogel particles were synthesized in supercritical methanol using a modified sol-gel process. The elaborated particles and the coated composite films were characterized by XRD, FTIR spectroscopy and by optical absorption. XRD patterns show a broadening of diffraction peaks of ZnO crystallites and a significant reduction in the intensity after their dispersion in silica. A reduction in lattice parameters was observed after the introduction of ZnO aerogel particles in silica. The Zn-O vibration bond strongly shifts to lower wavenumbers in composite films compared to the aerogel due to the formation of silica layerand successfully grafted over the ZnO nanoparticles. A strong Zn-O-Zn vibration bond is observed only in the spin-coated film. The blue shift observed in the absorption spectra indicates an enhancement in the optical band gap due to quantum confinement effect of ZnO nanoparticles when they are dispersed in silica matrix.

1. Introduction

In recent years, intensive research is conducted to find new physical properties of nanostructured materials. This is due to the specific optical and structural properties observed in nanomaterials, which lead to several new applications in photonic and photovoltaic.

The introduction of nanostructured materials in amorphous and transparent matrices is one of methods used to obtain high optical nonlinearity composite. These optical properties are strongly dependent on the structure of crystallite-matrix interface, chemical nature, size dispersion, size and morphology of the crystallites. The nanocomposite properties depend also on the nature and the form of the matrices (film or monolith) and on the synthesis method.

Zinc oxide (ZnO) is one of the most used materials due to its abundance in nature, its non-toxicity, broad and direct bandgap (3.37 eV) and its large exciton binding energy (60 meV). When incorporated in silica, ZnO nanoparticles have new behavior allowing them potential applications in photocatalysis [1], optoelectronics [2], optical and waveguiding materials [3,4], luminescent nanocomposites [5] and chemical sensors [6].

Several methods were employed to produce ZnO / silica nanocomposites as impregnating [7], ion implantation [8], physical vapor deposition (PVD) [9],chemical vapor deposition (CVD) [10], laser ablation [4], RF sputtering [11], liquid phase seeding [12] flame-assisted spray-drying method [13] and sol-gel [14,15].

To the best of our knowledge, zinc oxide aerogel particles synthesized in supercritical methanol and dispersed in silica matrix to obtain nanocomposite films have not been reported yet. So, in this paper, ZnO/silica composite films were elaborated by direct inclusion of small ZnO aerogel particles in liquid state silica. The guest particles were synthesized by modified sol-gel process in which the precursor solution was dried in supercritical conditions of temperature and pressure of methanol. Coatings deposition was carried out by dip-coating and spin-coating techniques on glass substrates. The structural and optical properties of the prepared aerogel and deposited nanocomposite films were studied and discussed.

2. Experimental procedures

2.1. Elaboration of ZnO aerogel powder

ZnO aerogel powder was prepared by dissolving zinc acetate dihydrate [[Zn (COOCH$_3$)$_2$.2H$_2$O]: 95% purity from Aldrich] in methanol under constant magnetic stirring for 10 min. After the complete dissociation of the precursor, the obtained

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solution was poured in one-liter capacity autoclave and 270 mL of methanol were added to the solution. This volume (270 mL) is the minimum volume required to reach the critical conditions of methanol with the used autoclave (79 bars, 240 °C). After cooling to room temperature, a white powder was recuperated and analyzed without any chemical or thermal treatments.

2.2. Elaboration of ZnO /silica composites

The obtained ZnO crystallites were directly dispersed in silica matrix. A mount of as-synthesized ZnO crystallites was introduced in ethanol under ultrasonic agitation at room temperature for 10 min in order to separate the agglomerated particles. The latter solution was left for sedimentation during one hour. The solution located near the free surface, which is supposed contain very small ZnO particles, was separated in order to use it in the preparation of the composites. Then, 20 mL of this solution were mixed with 7.5 mL of TEOS (Si $(OC_2H_5)_4$) and 3.33 mL of distilled water. The mixture was maintained under magnetic stirring at 40 °C for 20 min. After the gelling of the solution, composite films were deposited at room temperature on glass substrates. For the films deposition, we have used two techniques: spin-coating and dip-coating. The dip-coated films were obtained at pulling speed of 200 mm/min and have undergone 20 layer depositions. The drying was performed at 200 °C for 10 min after each layer deposition. The spin-coated monolayer film was deposited at 3000 rpm. Finally, all the prepared composite films were annealed in air at 500°C for 2 hours in a muffle furnace.

2.3. Characterizations

The studies of the crystal structure of ZnO aerogel and ZnO/silica nanocomposite films were carried out using a PanAnalytical diffractometer with Cu anode (wavelength 1.54 Å) at 40 kV and 30 mA. FT-IR spectra were recorded at room temperature on a Shimadzu Iraffinity-1 spectrometer. SEM image of ZnO aerogel was obtained by a scanning electron microscope type YEOL JSM-840A. UV–visible absorption spectra were recorded using a Safas UVmc2 spectrophotometer. Thermal gravimetric analysis (TGA) was carried out using a Netzsch STA 409 PC/PG instrument with a heating rate of 10 °C/min. The specific surface area and the pore size data of the as-synthesized ZnO aerogel were determined with Quantachrome Nova 2.2 instrument, by using nitrogen as adsorbate at liquid nitrogen temperature.

3. Results and discussion

The XRD spectrum of the as-prepared ZnO aerogel is shown in Figure 1a. The XRD patterns show that the sample is formed in single phase with hexagonal polycrystalline symmetry (JCPDSN ° 79-2205). The lattice parameters calculated from the XRD pattern are a = 0.3253 nm and c = 0.5211 nm. The Zn-O bond length in the elaborated sample was found to be 0.1979 nm. The crystallites size, calculated using the well-known Scherer's formula, was found to be between 17 and 28 nm (estimated from the line width of all the XRD peaks) with an average of 22 nm. To study the morphology of the sample, the as-synthesized ZnO aerogel was examined using scanning electron microscope (SEM). The SEM image, illustrated in Figure 1b, reveals that most of the ZnO particles are quasi-spherical and the grains are less condensed. This result indicates that supercritical drying in methanol leads to produce ZnO particles with less agglomeration yield (low density) with high porosity compared with those prepared in supercritical ethanol [16,17]. In order to study the textural properties of the aerogel, nitrogen adsorption desorption analysis at 77 K has been performed. The specific surface area was determined by applying the Bruneauer-Emmett-Teller (BET)
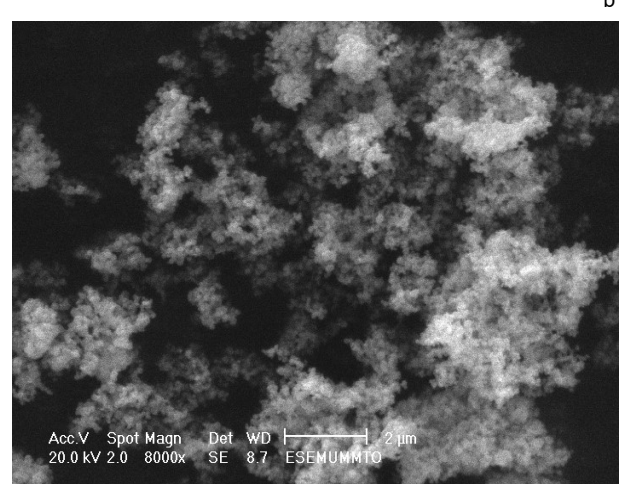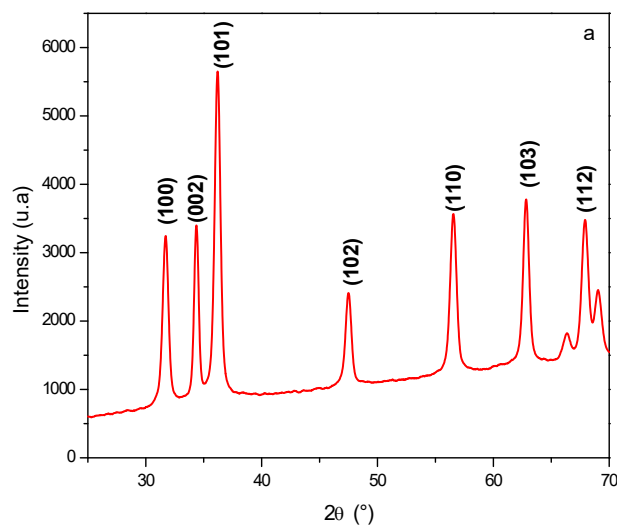

Fig. 1 - XRD spectrum (a) and SEM image (b) of the as-prepared ZnO aerogel elaborated in supercritical methanol.
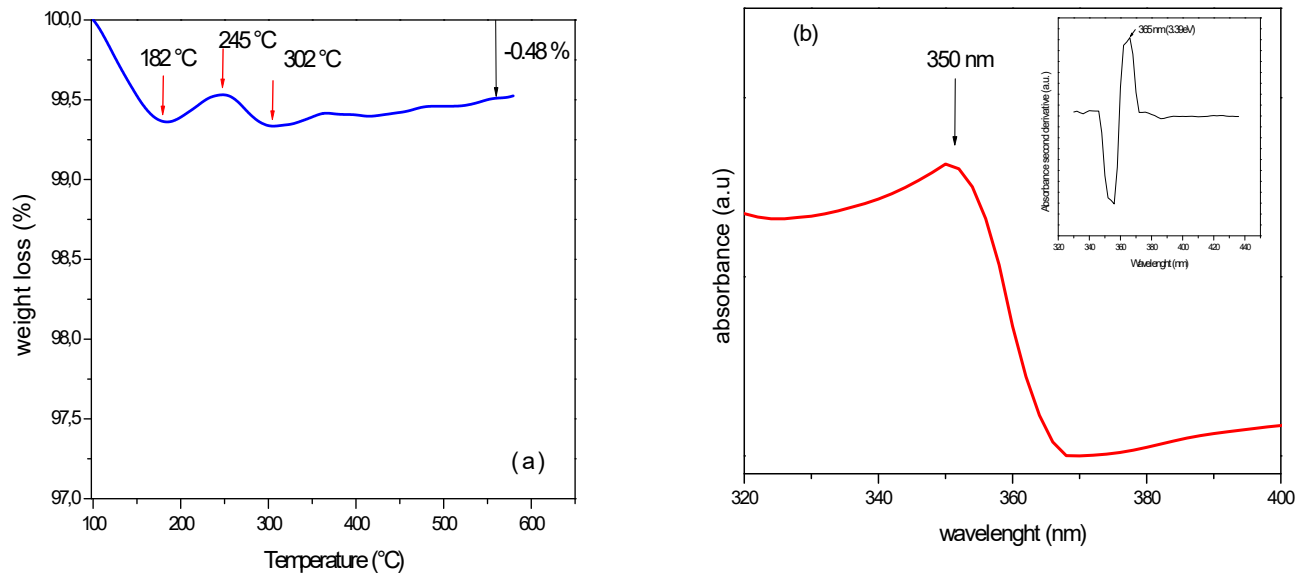
Fig. 2 - TGA curve (a) and optical absorption (b) of the as-prepared ZnO aerogel elaborated in supercritical methanol.

method and found to be 18.815 m^2/g. The total pore volume, considering only the smaller pores (radius less than 648 Å) , is about 0.086 cm^3/g. Pore size data (BJH method) were determined using de Boer calculation method (programme Quantachrome NovaWin2 - Data Acquisition and Reduction for NOVA instruments). The found values of the pore surface area (S$_{BJH}$), pore volume (V$_p$) and pore radius (R$_p$) are 11.69 m^2/g, 0.036 cm^3/g and 20.6 Å, respectively. Assuming that the particles have solid, spherical shape and same size, the surface area can be related to the average equivalent particle size by the empirical equation[18] :

$$D_{BET} = \frac{6000}{\rho_{ZnO} \cdot S_{BET}}$$

Where D_{BET} is the mean crystalline size (in nm) of the particles, ρ_{ZnO} is the density of ZnO powder (5.60 g/cm^3) and S_{BET} is the BET specific surface area (m^2/g). By applying this equation, D_{BET} value of 57 nm was obtained for the aerogel. The discrepancy between ZnO crystallites sizes determined by porous structure (BET) and crystalline structure (XRD) measurements indicated that there is agglomeration in the ZnO aerogel particles [18]. In our case, the ZnO particles synthesized in supercritical methanol have high specific surface area and low degree of aggregation compared to those obtained with others synthesis methods [19 - 21].

To study the thermal stability and the purity of the synthesized ZnO aerogel, TGA measurements were carried out. Mass loss (TGA) curve of the as-synthesized ZnO aerogel with heating up to 600 °C is presented in Figure 2 (a). The TGA curve shows a relatively very small weight loss in the temperatures rage 100-180°C, which is mainly attributed to the evaporation of surface adsorbed water. The second mass loss observed between 245 and 302 °C is probably due to residual organic compounds present in very small amounts

in the aerogel. An increase in mass is also observed between 180 and 245 °C. This increase is probably due to the formation of new products after the interaction of unreacted acetate with the atmospheric gases. The global mass loss after annealing to 600 °C does not exceed 0.48 %. This clearly indicates that the synthesized aerogel has extreme purity. In the other hand, we can consider that the aerogel mass variation in the high temperatures range is too small as to fall into the experimental error limits.

The UV-visible properties of the elaborated aerogel have been studied and the optical absorption spectrum of the sample is shown in Figure 2(b). The small particle size diameter is confirmed by the position of the absorption band at 350 nm [22]. We note a distinct blue shift of absorption profile, which occurs in this aerogel as its absorption peak shifts to short wavelength side in comparison with that of bulk ZnO [23]. This behavior can be attributed to the size reduction effect of ZnO aerogel synthesized in supercritical methanol. The band gap value estimated from the second derivative curve of the absorbance is found to be about 3.39 eV.

The XRD spectra of ZnO aerogel/silica composite films deposited by dip and spin-coating techniques and that of ZnO aerogel (for comparison) annealed at the same conditions (500 °C for 2 hours) are shown in Figure 3. After the introduction of ZnO crystallites in silica matrix, we note an enlargement of the diffraction peaks and a considerable decrease in intensity compared with that of ZnO aerogel. This enlargement is due to the very small size of the aerogel particles dispersed in the near free surface solution after sedimentation. This method may be very effective to disperse nanometric-sized particles in transparent and amorphous host matrices. The XRD spectra of ZnO/silica films indicate that the characteristics
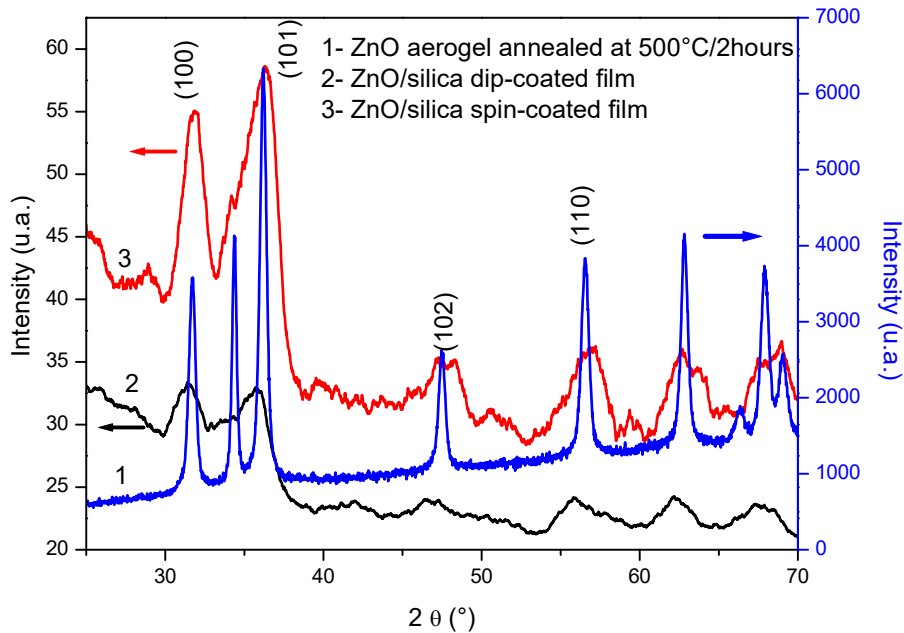
Fig. 3 - XRD spectra of annealed ZnO aeorgel (1), ZnO / silica dip-coated nanocomposite film (2) and ZnO / silica spin-coated nanocomposite film (3).

Table 1

Lattice parameters (*a* and *c*), Zn-O length (*L*) and crystallites size (*D*) of ZnO aerogels

Sample	a (Å)	c (Å)	L (Zn-O) (nm)	Crystallite size D (nm)
As-prepared ZnO aerogel	3.2532	5.2113	0.1979	22
Annealed ZnO aerogel	3.2661	5.2358	0.1988	24
ZnO/silica dip-coated film	3.2519	5.2276	0.1982	5
ZnO/silica spin-coated film	3.2501	5.2187	0.1977	7

peaks are still in accordance with the wurtzite phase of ZnO, confirming that silica coating does not influence the crystalline structure of ZnO aerogel nanoparticles.

In silica matrix, the diffraction peaks (002) and (101) are so large that they form a unique band due to the overlapping of their intensities. The spin-coated ZnO/silica composite film spectrum shows better crystalline quality and a relatively high concentration of ZnO particles compared to the dip-coated ones. This result shows that ZnO crystallites sediment rapidly during dip-coating process and only few particles remain in the layer. The low viscosity of the solution could explain this phenomenon.

The crystallite size, estimated by the Scherrer formula, after a Gaussian multi-peaks fit of the most pronounced XDR peaks, is found to be 7 nm in the spin-coated film and 5 nm in the dip-coated one. This means that the biggest particles sediment rapidly during the drawing process. The lattice parameters calculated for the dip-coated film are found to be $a = 3.2519$ Å and $c = 5.2276$ Å . These values are found to be $a = 3.2501$ Å and $c = 5.2187$ Å in the spin-coated film. After annealing at 500°C for 2 hours, the ZnO aerogel lattice parameters become $a = 3.2661$ Å and $c = 5.2358$ Å . The Zn-O bond length in the films is found to be 0.1977, 0.1982 and 0.1988 nm in spin-coated film, dip-coated film and annealed aerogel, respectively. All calculated parameters are summarized in Table 1. These results indicate that silica exerts a compression effect (stress) on ZnO crystallites, which leads to a reduction in Zn-O length and lattice parameters.

The infrared spectra (FTIR) of the prepared nanocomposite films are presented in Figure 4. For ZnO aerogel, a large band, due to Zn-O vibration bond, is observed at 470-570 cm^{-1}. The absorption band at 1130 cm^{-1} is assigned to the vibration ν (C = O) due to the presence of carbon groups in the aerogel during annealing. For ZnO / silica films annealed at 500 ° C for 2 hours, no bands due to the presence of carboxylic groups are observed.
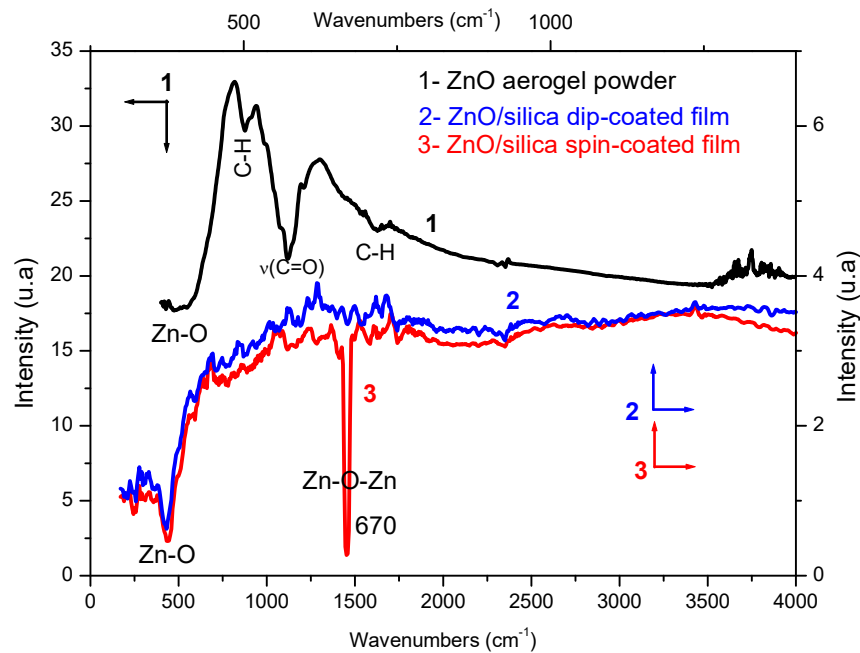
Fig.4 - XRD spectra of ZnO aeorgel (1), ZnO / silica dip-coated nanocomposite   film (2) and ZnO / silica spin-coated nanocomposite film (3).

However, the Zn-O vibration bond is observed at 370 cm^{-1} and 377 cm^{-1} in ZnO/silica dip-coated and spin-coated film, respectively. A strong absorption band related to Zn-O-Zn vibration bond, is observed in the spectrum of the ZnO / silica composite film deposited by spin coating at about 670 cm^{-1} [24]. This band appears also in the dip-coated film FTIR spectrum but with very low intensity. The authors of the work [24] reported that the observed stretching vibration is observed at an annealing temperature higher than 500 °C and it is indicative of a good distribution of ZnO crystallites into silica matrix. El Nahhal and co-workers [23] reported that the intensity of the bands due to Si-O-Si vibration at 450-500 cm^{-1} strongly decreases in ZnO/SiO$_2$ IR spectrum compared to pure silica. They suggest that this reduction in intensity leads to the formation of Si-ZnO bond. The formation of this bond manifests the existence of a silica layer and successfully grafted over the ZnO nanoparticles. In our spectra, no remarkable bands in the range 450-500 cm^{-1} are observed. This can explain the shift of Zn-O vibration bond to lower wavenumbers after the introduction of ZnO particles in silica matrix.

The optical absorption spectra of elaborated composite films are illustrated in Figure 5. The peaks at 272 nm (4.55 eV) and 265 nm (4.67 eV) observed respectively in spin-coated and dip-coated ZnO/silica composite films reflect the excitonic nature of the transitions and the discretization of the energy levels characteristic of nanocrystals [25]. This massive blueshift to shorter wavelength in the absorption spectra (compared to the bulk ZnO) is probably due to the decrease in size of ZnO nanoparticles embedded in silica matrix. The band at 375 nm (3.31 eV), observed only in ZnO/silica spin-coated film, is due to the band to band transi-
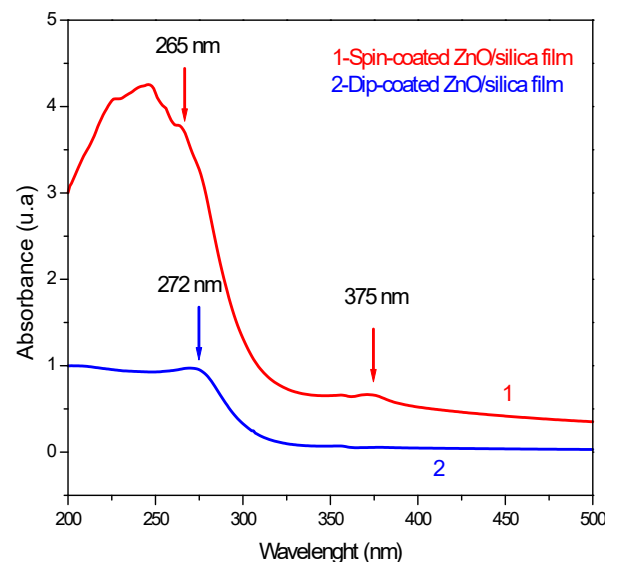

Fig.5 - Optical absorption spectra of ZnO / silica composite films deposited by spin-coating (1) and dip-coating (2) techniques.

tion and reflects the non-dissociation ZnO crystallites after their introduction into the silica.

4. Conclusion

ZnO aerogel crystallites were synthesized in supercritical methanol by a modified sol-gel process. The smaller particles were selected by sedimentation and directly dispersed in liquid state silica . ZnO / silica nanocomposite films were deposited on glass substrates by dip-coating and spin-coating techniques. ZnO aerogel crystallites are in wurtzite structure with excellent purity and have 22 nm average crystallites size. SEM image shows less agglomerated quasi-spherical ZnO

crystallites. The deposited ZnO/silica composite films are transparent and the ZnO particles in the silica have a size of 5 and 7 nm in the dip-coated and spin-coated films, respectively. Infrared band of the Zn-O bond shifts to smaller wavenumbers after the dispersion of ZnO crystallites in silica matrix. A strong Zn-O-Zn vibration band was observed only in ZnO/silica spin-coated composite film. The blue shift observed in the absorption spectra indicates an enhancement in the optical bandgap due to quantum confinement effect of ZnO nanoparticles when they were dispersed in silica matrix. The use of ZnO aerogel particles elaborated in supercritical methanol as solute in silica solution leads to obtain very interesting composite materials for further applications in photonics and optoelectronic devices.

REFERENCES

1. I. A. Siddiquey T. Furusawa , M. Sato, N. Suzuki, Microwave-assisted silica coating and photocatalytic activities of ZnO nanoparticles, Materials Research Bulletin ,2008, **43**, 3416.
2. S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, Recent progress and properties of ZnO, *Progress in Materials Science.* 2005, **50,** 293.
3. T. Chen, T. Rajh, Z.Y. Wang, M.C. Thurnauer, XAFS studies of surface structures of TiO2 nanoparticles and photocatalytics reduction of metal ions, Journal of Physical Chemistry,1997,**101,**10688.
4. W.S. Hu , Z.G. Liu , X.L. Guo , C. Lin , S.N. Zhu , D. Feng , Preparation of c-axis oriented ZnO optical waveguiding films on fused silica by pulsed laser reactive ablation, Materials Letters,1995, **25,**5.
5. C. Bouvy, W. Marine, Bao-Lian Su, ZnO/mesoporous silica nanocomposites prepared by the reverse micelle and the colloidal methods: Photoluminescent properties and quantum size effect, Chemical Physics Letters, 2007, **438**, 67.
6. N. Carmona, E. Herrero, J. Llopis, M.A. Villegas, Chemical sol-gel based sensors for evaluation of environmental humidity, Sensors and Actuators ,2007,**B 126** , 455.
7. C. Cannas, M. Mainas, A. Musinu, G. Piccaluga, ZnO/SiO$_2$ nanocomposites obtained by impregnation of mesoporous silica, Composites Science and Technology,**63** ,1187.
8. Y.X. Liu, Y.C. Liu, D.Z. Shen, G.Z. Zhong, X.W. Fan, X.G. Kong, R. Mu, D.O. Henderson The structure and photoluminescence of ZnO films prepared by post-thermal annealing zinc-implanted silica, Journal of Crystal Growth, 2002,**240** , 152.
9. S. Yang, H.C. Hsu, W.R. Liu, H.M. Cheng, W.F.Hsieh, Correlation between photoluminescence and varied growth pressure of well-aligned ZnO nanorods on fused silica substrate, Optical Materials, 2007,**30** ,502.
10. W. Zeng , Z. Wang, X.F. Qian , J. Yin , Z.K. Zhu, ZnO clusters in situ generated inside mesoporous silica, Materials Research Bulletin, 2006,**41** (2006) ,1155.
11. Y.Y. Peng, T.E.Hsieh,C.H. Hsu,White-light emitting ZnO–SiO2 nanocomposite thin films prepared by the target-attached sputtering method, Nanotechnology, 2006, **17 (1)** 174.
12. D. Djouadi , A. Chelouche, A. Aksas , M. Sebais, Optical properties of ZnO/silica nanocomposites prepared by sol-gel method and deposited by dip-coating technique, Physics Procedia,2009, **2**,701.
13. G.Yu. Rudko, S.A. Kovalenko, E.G. Gule, V.V. Bobyk, V.M. Solomakha, A.B. Bogoslovskaya, Zinc oxide nanoparticles fabricated in the porous silica matrix by the sublimation method, Semiconductor Physics, Quantum Electronics & Optoelectronics, 2015, **18(1)**, 20.
14. K. Khosravy, P. Sangpour,Effect of grain size on transmittance and wettability of nanocomposites thin films ZnO-SiO$_2$ prepared by sol gel, International Materials Physics Journal, 2014,**2(1)**, 21.
15. L.Shastri, M.S. Qureshi, M.M. Malik, Photoluminescence study of ZnO/SiO$_2$ nanostructures grown in silica matrix obtained via sol-gel method, Journal of Physics and Chemistry of Solids, 2012,**74(4)** , 595.
16. D. Djouadi ,A. Aksas, A. Chelouche, Elaboration ,structural and optical characterization of ZnO nanotorus crystallites . Annales de Chimie-Science des Matériaux ,2010 ,**35 (5)**, 255.
17. M. Meddouri, D. Djouadi, A. Chelouche, T. Touam, A.Chergui, Effect of co-solvent on structural and morphological properties of ZnO aerogel prepared by a modified sol-gel process, The European Physical Journal – Applied Physiqcs, 2014, **66**, 10402 .
18. D. Raoufi, Synthesis and microstructural properties of ZnO nanoparticles prepared by precipitation method, Renewable Energy, 2013, **50**, 932.
19. A. Aimable, M. T. Buscaglia, V. Buscaglia, P. Bowen, Polymer-assisted precipitation of ZnO nanoparticles with narrow particle size distribution, Journal of the European Ceramic Society, 2010,**30** , 591.
20. A. Kołodziejczak-Radzimska, T. Jesionowski, Zinc Oxide—From Synthesis to Application: A Review, Materials ,2014, **7**, 2833.
21. B. Veriansyah, J.D. Kim, B. K. Min, Y. H.Shin,Y.W. Lee, J. Kim, Continuous synthesis of surface-modified zinc oxide nanoparticles in supercritical methanol, The Journal of Supercritical Fluids,2010, 52(1),76.
22. E.A. Meulenkamp, Synthesis and Growth of ZnO Nanoparticles, The Journal of Physical Chemistry B ,1998, **B102** , 5566.
23. I. M. El-Nahhal, J. K. Salem, S. Kuhn,T.Hammad, R.Hempelmann, S. Al Bhaisi , Synthesis & characterization of silica coated and functionalized silica coated zinc oxide nanomaterials, Powder Technology,2016, **287** , 439.
24. A. Mossad Ali, A. A. Ismail, R. Najmy, A. Al-Hajry, Annealing effects on zinc oxide-silica films prepared by sol–gel technique for chemical sensing applications, Thin Solid Films,2014,**558**, 378.
25. R. Moleski, E. Leontidis, F. Krumeich, Controlled production of ZnO nanoparticles from zinc glycerolate in a sol–gel silica matrix, Journal of Colloid and Interface Science, 2006,**302** ,246.

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