Bulgarian Chemical Communications, Volume 48, Special Issue G (pp. 188-192) 2016

Optical properties of ZnO thin films deposited by the method of electrospray

G. Marinov[1,2], M. Vasileva[1], V. Strijkova[1], N. Malinowski[1] and T. Babeva[1]*

[1]*Institute of Optical Materials and Technologies ''Acad. J. Malinowski'', Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria*
[2] *TACK Laboratory, 2 Ivan Peev Marusha str., Pravetz, Bulgaria*

Received October 10, 2016; Revised November 20, 2016

ZnO films with thicknesses in the range 60-220 nm were prepared by electrospray method on silicon substrates at temperature of 200 ºC using electrostatic set-up with vertical configuration and preliminarily optimized sol-gel recipe including zinc acetate dehydrate as a precursor and ethanol as a solvent. The thin films were subjected to high temperature (550 ºC) post annealing. The deposition voltage and distance between the emitter and collector were varied in the range 9.5 – 13.5 kV and 4 – 7 cm, respectively. The surface topography and roughness were measured by Atomic Force Microscope (AFM) and optical profiler. Optical constants and thickness of the films were calculated from reflectance spectra using nonlinear curve fitting. Photoluminescence spectra were measured at room temperature at excitation wavelength of 335 nm. The influence of deposition parameters and post annealing on surface morphology, optical properties and photoluminescence of thin ZnO films was discussed.

Keywords: ZnO films, electrospray, sol-gel, optical properties.

INTRODUCTION

ZnO is a wide band semiconductor with large exciton binding energy. Due to its transparency in UV and NIR ranges, electro and elasto-optical properties, low resistivity, biocompatibility, low cost and long-term stability, ZnO is an attractive material for utilization in various modern devices such as biosensors [1], optical gas sensors [2], piezoelectric sensors [3], optoelectronics [4], transducers and resonators [5], integrated optical devices [6], etc. ZnO thin films are interesting transparent conducting oxides and are regarded as an alternative material to the widely used ITO for optically transparent electrodes in flat panel displays [7] or solar cells [8].

Different physical and chemical methods of ZnO films deposition have already been implemented: rf sputtering [9], pulsed laser deposition [2], plasma enhanced chemical vapor deposition [10], spray pyrolysis [11], sol–gel process [12], molecular beam epitaxy [13], atomic layer deposition [14], electrospray [15], etc.

However, in order to realize high-performance ZnO based devices, it will be a real advantage to grow high quality ZnO thin films with controllable parameters using easy and low cost methods. Sol-gel process emerges as a convenient, efficient and inexpensive technique for thin film preparation, enabling tailored properties and easy doping option at molecular level [12]. Besides, it could be successfully combined with electrospray method for film deposition having advantages of simple setup, low cost and easy control of morphology and stoichiometry. Tailored structural and optical parameters could be achieved simply by variation of applied voltage and substrate temperature [15, 16]. However, for effective technological applications of ZnO films, the impact of different preparation conditions on the film properties have to be thoroughly investigated and mutual relationships to be revealed.

In this paper we combine the advantages of both sol-gel and electrospray methods in order to deposit high quality ZnO thin films with controllable properties. The influence of deposition parameters and post annealing on surface morphology, optical properties and photoluminescence of thin ZnO films is discussed.

EXPERIMENTAL DETAILS

The sol-gel method was used for preparation of solution for electrospray. 0.115 g of zinc acetate dehydrate was dissolved in 0.5 ml H_2O and 3.5 ml ethanol and stirred at room temperature for 2 hours. Two drops of acetic acid were added as

* To whom all correspondence should be sent:
E-mail: babeva@iomt.bas.bg

stabilizers. Prior to the deposition the solution was aged for 24 h at room temperature. All chemicals (Sigma Aldrich) were of analytical reagent grades and used without further purification.

The deposition of thin film was performed using an electrostatic set-up with vertical configuration equipped with home-made heater capable of maintaining the substrate temperature up to 300 ºC in controllable manner (Fig. 1).

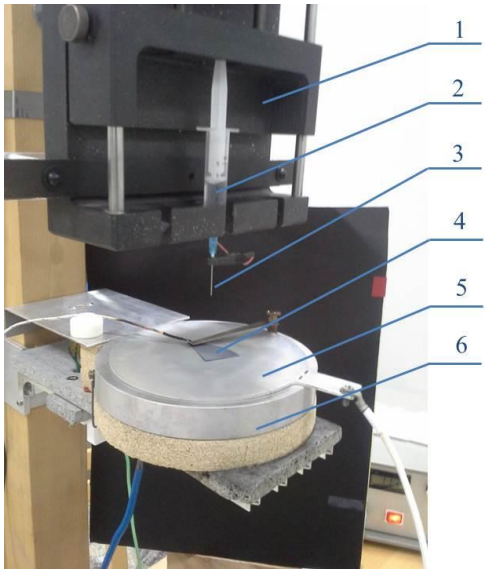

Fig. 1. Vertically configured electrospraying set-up consisting of syringe pump (1), 5 ml syringe with Zn sol (2), emitter (3), substrate (4), collector (5) and heater (6).

The emitter of the electrospraying set-up was a 5 ml syringe with stainless steel needle of inner diameter of 0.3 mm and length of 32 mm and the collector is the stainless steel-duralumin plate put on the heater and grounded in a save way. The distance between the emitter and collector was 4 cm and 7 cm and a high voltage of 9.5 kV and 11 kV in the first case and 12.5 and 13.5 kV in the second one was applied via a DC power supply (Applied Kilovolts, UK). For all films the substrate temperature is kept at 200 ºC. Fig. 1 shows a picture of the electrospray set-up.

The surface morphology and roughness of the films were characterized by Atomic Force Microscopy (MFP-3D, Asylum Research, Oxford Instruments), while the dispersion of the droplets over the substrate and the variation of their size with deposition conditions were examined by crossed-polarizer optical profilometry (Zeta-20, Zeta Instruments).

The refractive index (n) and extinction coefficient (k) along with the thickness (d) of the films were determined from reflectance spectra of the films measured at normal light incidence by UV-VIS-NIR spectrophotometer Cary 05E (Varian, Australia) using non-linear curve fitting method [17]. The experimental errors for n, k and d were 0.005, 0.003 and 2 nm, respectively.

The photoluminescence spectra of the films were taken at room temperature at excitation wavelength of 335 nm using spectrofluorometer FluoroLog3-22 (Horiba JobinYvon).

RESULTS AND DISCUSSIONS

The typical surface morphology of the electrosprayed ZnO films is illustrated in Fig. 2 by AFM images of the as-deposited ZnO films. All films are crack-free and have similar surface morphology comprising spherical grains that are tightly packed and distributed uniformly over the entire film surface. For all films the size of the grains is similar varying in the range 50 – 500 nm and no effect of post-annealing on the grains size is observed (Fig. 3). The thickness of the films deposited at 4 cm is 220 nm, while those at 7 cm are 60 nm thick.

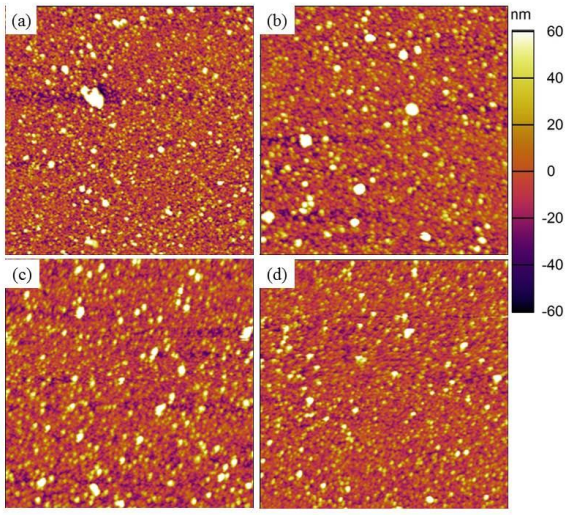

Fig. 2. AFM pictures (10 µm x 10 µm) of the surface of ZnO films deposited on Si-substrate by the electrospray method at applied voltage of 9.5 kV (a), 11 kV (b), 12.5 kV (c) and 13.5 kV (d) and an emitter-to-collector distance of 4 cm (a, b) and 7 cm (c, d).

After annealing a weak smoothing of the surface takes place for films deposited at a distance of 4 cm (Fig. 4 (a)), while a slight roughening is observed for these at 7 cm (Fig. 4 (b)). The typical rms roughness values of 16 – 19 nm are obtained for the films that are consistent with those measured for spin- and dip-coated films [18, 19]. The weak smoothing with distance illustrated in Fig. 3 could be due to a smaller

thickness of the films obtained at a distance of 7 cm.

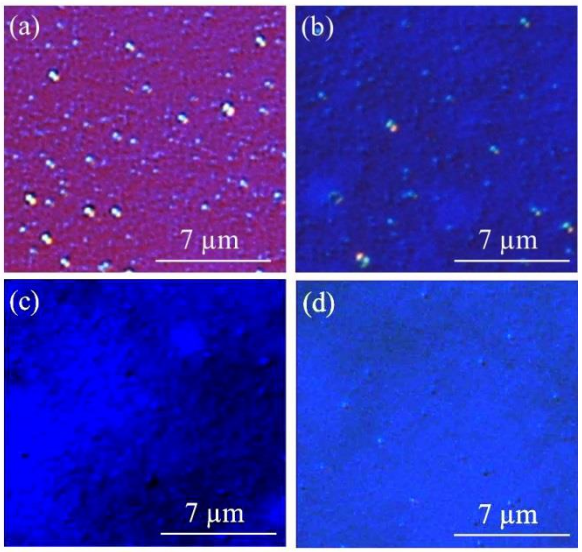

Fig. 3. Optical microscopic images of electrosprayed ZnO using applied voltage of 9.5 kV (a,b) and 13.5 kV (c,d), emitter-to-collector distance of 4 cm (a,b) and 7 cm (c,d) before (a, c) and after annealing at 550 ºC (b,d).

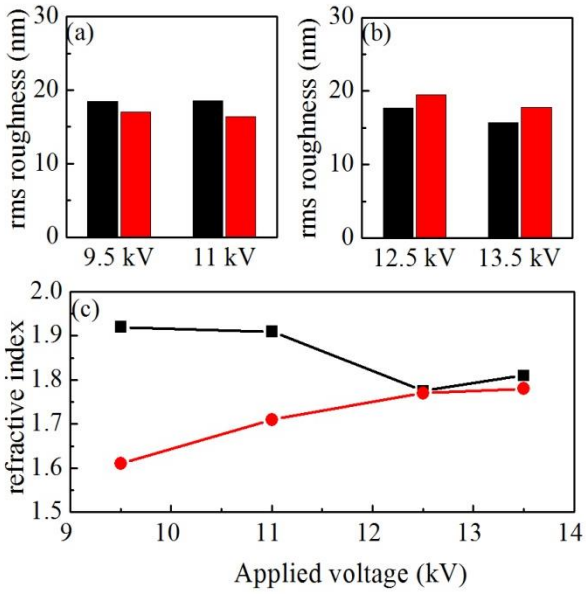

Fig. 4. Surface roughness (rms) in [nm] of ZnO films deposited at emitter-to-collector distance of 4 cm (a) and 7 cm (b) and refractive index at wavelength of 600 nm as a function of applied voltage (c) for as-deposited (black color) and annealed films (red color).

As the distance between the emitter and collector increases from 4 cm to 7 cm a reduction in deposition rate from 5 nm.min^{-1} to 3 nm.min^{-1} is observed which is due to the enlargement of the covered surface area. The increase of applied voltage at fixed distance leads also to a weak decrease of deposition rate. Besides, a strong lateral thickness gradient is detected for deposition distance of 4 cm unaffected by the applied voltage, while the area of uniform film thickness expands considerably when the deposition is carried out at a distance of 7 cm.

The calculated values of refractive index (n) of the films as functions of applied voltage are presented in Fig. 4 (c). The curves for as-deposited and annealed films show opposite trends: a decrease in n is observed for as-deposited films while after annealing n for the films increases with voltage reaching steady-state at applied voltage greater than 12.5 kV. For all films the post-deposition annealing leads to the reduction of n mostly pronounced for the films deposited at a distance of 4 cm. As shown in [20] the decomposition of zinc acetate occurs for temperature greater than 400 ºC. Considering that during the electrospray the substrates are kept at 200 ºC it may be expected the as-deposited films to have nonstoichiometric composition due to the residual non-reacted zinc acetate as opposite to the annealed one wherein the thermal decomposition of zinc acetate should be completed. Thus, the difference in chemical composition could be the reason for the change in refractive index after annealing. It is possible the process of organic decomposition to be favored in the case of thinner films (deposited at a distance of 7 cm). As a result it may happen the zinc acetate residual in them to be less as compared to thicker films (deposited at a distance of 4 cm) and their refractive index before annealing to be closer to n for the annealed ones (Fig. 4(c)).

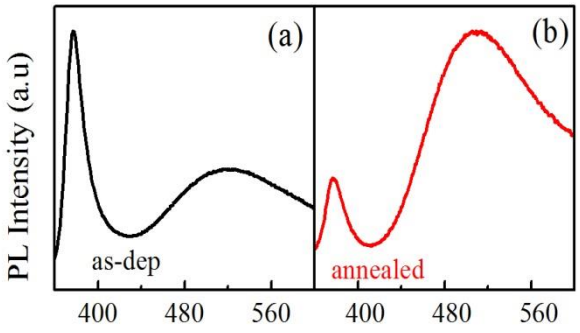

Fig. 5. Room temperature photoluminescence spectra of as-deposited (a) and annealed (b) ZnO films taken at excitation wavelength of 335 nm.

The photoluminescence spectra at room temperature and excitation wavelength of 335 nm of as-deposited and annealed ZnO films are presented in Fig. 5. A narrow UV emission peak

and a broad green emission peak with different relative intensities are observed in both cases. The first one, centered at 377 nm (3.29 eV) is ascribed to the inter-band radiation recombination of photo-generated electrons and holes [21-23]. Usually the light emitted due to the free exciton recombination has an energy equal to or slightly greater than the optical band gap, that for the case of sol-gel ZnO films is in the range 3.20 – 3.30 eV [21, 22]. The broad green emission, centered at 520 nm (2.38 eV) for the as-deposited films and at 510 nm (2.43 eV) for the annealed ones, with energy smaller than the band gap should correspond to the transition between band edges and the local levels in the band gap. The last are formed by some defects in ZnO [24], for example zinc and oxygen vacancies, interstitial zinc, interstitial oxygen, etc. [23, 25]. According to Yu et. al. [26] the stronger green emission relative to UV emission in the case of annealed films suggests that there is a great fraction of oxygen vacancies in the films. They may originate from oxygen deficiency due to the high temperature annealing of films in ambient atmosphere. Further experiments are required for clarification of the exact reason.

CONCLUSIONS

The successful application of electrospray method with vertical set-up for deposition of ZnO thin films is demonstrated. The applied voltage is varied between 9.5 kV and 13.5 kV, while the emitter-to-collector distance is fixed at 4 cm and 7 cm. The deposition parameters and annealing do not influence substantially the surface topography of the films, while after annealing a weak smoothing is observed for films deposited at 4 cm and roughening – for films at 7 cm. In order to obtain broad area of uniform thickness the deposition should be carried out at a higher distance and lower applied voltage. Further, the refractive index increases as the applied voltage increases. The denser ZnO films are obtained at the highest applied voltage (1.78 at wavelength of 600 nm). A narrow UV emission peak and a broad green emission peak with different relative intensities are observed for as deposited and annealed ZnO films assigned to the free exciton recombination and oxygen vacancies, respectively.

Acknowledgement: *The financial support from the National Science Find – Bulgaria (project DFNI-T02/26) is highly appreciated.*

REFERENCES

1. A. Ansari, M. Khan, M. Alhoshan, S. Alrokayan, M. Alsalhi, *J. Semicond.*, **33**, 42002-1 (2012).
2. A. Dikovska, P. Atanasov, S. Tonchev, J. Ferreira, L. Escoubas, *Sens. Actuators A: Phys.*, **140**, 19 2007.
3. M. Arnold, P. Avouris, Z. Pan, Z. Wang, *J. Phys. Chem. B*, **107**, 659 (2003).
4. H. Sun, Q. Zhang, J. Wu, *Nanotechnology*, **17**, 2271 (2006).
5. C. Klingshirn, *Chem. Phys. Chem*, **8**, 782 (2007).
6. R. Heideman, P. Lambeck, J. Gardeniers, *Opt. Mat.*, **4**, 741 (1995).
7. T. Hirao, M. Furuta, H. Furuta, T. Matsuda, T. Hiramatsu, H. Hokari, M. Yoshida, H. Ishii, M. Kakegawa, *J. Soc. Inf. Display*, **15**, 17 (2007).
8. K. Kushiya, M. Ohshita, I. Hara, Y. Tanaka, B. Sang, Y. Nagoya, M. Tachiyuki, O. Yamase, *En. Mat. Sol. Cells*, **75**, 171 (2003).
9. M.-S. Wu, W.-C. Shih, W.-H. Tsai, *J. Phys. D. Appl. Phys*., **31**, 943 (1998).
10. S. Kitova, G. Danev, *J. Phys.: Conf. Ser*., **223**, ID 012022 (2010).
11. O. Dimitrov, D. Nesheva,V. Blaskov, I. Stambolova, S. Vassilev, Z. Levi ,V. Tonchev, *Mater. Chem. Phys*., **148**, 712 (2014).
12. L. Znaidi, *Mat. Sci. Eng. B*, **174**, 18 (2010).
13. K. Nakamura, T. Shoji, K. Hee-Bog, *Jpn. J. Appl. Phys. Lett*. **39**, 534 (2000).
14. B. Blagoev, D. Z. Dimitrov, V. Mehandzhiev, D. Kovacheva, P. Terziyska, J. Pavlic, K Lovchinov, E. Mateev, J. Leclercq, P. Sveshtarov, *J. Phys.: Conf. Ser*., **700**, ID 012040, (2016).
15. A. Hosseinmardi, N. Shojaee , M. Keyanpour-Rad, T. Ebadzadeh, *Ceram. Int*., **38**, 1975 (2012).
16. K.-S. Hwang, J.-H. Jeong, Y.-S. Jeon, K.-O. Jeon, B.-H. Kim, *Ceram. Int*., **33**, 505 (2007).
17. K. Lazarova, M. Vasileva, G. Marinov and T. Babeva, *Opt. Laser Technol.*, **58**, 114 (2014).
18. B. Shivaraj, H. Murthy, M. Krishna, B. Satyanarayana, *Procedia Mater. Sci.*, **10**, 292 (2015).
19. S. Singh, P. Chakrabarti, *Superlattices and Microstruct.*, **64**, 283 (2013).
20 Y. Ding, P. Zhang, Y. Jiang, F. Xu, J. Chen, H. Zheng, *Solid State Phenom.*, **155**, 151 (2009).
21. F. Ghodsi, H. Absalan, *Acta Phys. Pol. A*, **118**, 659 (2010).
22. Z. Khan, M. Khan, M. Zulfequar, M. Shahid Khan, *Mat. Sci. Appl*., **2**, 340 (2011).
23. Y.-S. Kim, W.-P. Tai, S.-J. Shu, *Thin Solid Films*, **491**, 153 (2005).
24. B. Lin, Z. Fu, Y. Jia, G. Liao, *J. Electrochem. Soc.*, **148**, G110 (2001).

25. K. Vanheusden, W. Warren, C. Seager, D. Tallant, J. Voigt, B. Gnade, *J. Appl. Phys.* 79, 7983 (1996).

26. K. Yu, Y. Zhang, L. Luo, W. Wang, Z. Zhu, J. Wang, Y. Cui, H. Ma, W. Lu, *Appl. Phys. A*, **79**, 443 (2004).

ОПТИЧНИ СВОЙСТВА НА ТЪНКИ ФИЛМИ ОТ ZnO, ПОЛУЧЕНИ ЧРЕЗ ЕЛЕКТРО-СПРЕЙ

Г. Маринов[1,2], М. Василева[1], В. Стрижкова[1], Н. Малиновски[1] и Цв. Бабева[1]

[1]Институт по оптически материали и технологии ''Акад. Й. Малиновски", Българска Академия на Науките, ул. "Акад. Г. Бончев", блок 109, 1113, София, България
[2] ТАСК Лаборатория, ул. "Иван Пеев Маруша" №2, Правец, България

Постъпила на 10 октомври 2016 г.; коригирана на 20 ноември, 2016 г.

(Резюме)

Изследвани са тънки слоеве от ZnO с дебелини в диапазона 60-220 нм, получени чрез метода на вертикален електро-спрей върху подложки от кристален силиций при температура на подложката 200 °C. Съставът на използвания зол, състоящ се от цинков ацетат дехидрат като прекурсор и етанол като разтворител, е предварително оптимизиран. След отлагане филмите са загряти на 550 °C за 2 часа. Подаваното напрежение и разстоянието между емитера и колектора са варирани в диапазона 9.5 – 13.5 kV и 4 – 7 cm, съответно. Топографията и грапавостта на повърхността са измерени чрез AFM и оптичен профиломер. Оптичните константи и дебелината на филмите са изчислени от спектрите на отражение чрез нелинейно минимизиране. Измерена е фотолуминесценцията при стайна температура. Дискутирано е влиянието на параметрите на отлагане и загряването след отлагане върху повърхностната морфология, оптичните свойства и фотолуминесценцията на тънки слоеве от ZnO.