The thickness effect of ZnO thin films on optical Properties deposited by spray pyrolysis

Farid Khediri [1], Abdekader Hafdallah [1] and Mouna Bouhelal [1]

[1]*Applied and Theoretical Physics Laboratory, Department of Material Sciences, University Larbi Tebessi - Tebessa, 12002 Tebessa, Algeria*

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khediri_adel@yahoo.fr

***Abstract*—Much attention has been lead up the transparent conducting oxides (TCOs) in recent years due to their interesting physical properties, which combine electrical conductivity and optical transparency in the spectral range of the visible. Among these oxides zinc oxide ZnO is with the properties optical and electric has attracted the attention of researchers for a long time. In this work Zinc oxide thin films prepared by spray pyrolysis technique. A set of ZnO thin films were deposited with various deposition time, on glass substrate at 350 °C. The precursor solution is formed with zinc acetate in distilled methanol with 0.1 molarity. The deposition time was ranged from 2 to 8 min. The optical properties of those films were examined by ultraviolet-visible spectrometer (UV). ZnO thin films were highly transparent in the visible with the maximum transmittance of 85% and the optical band gap was found between 3.25 and 3.28 eV.**

Keywords—Spray pyrolysis, Zinc oxide, thin films, optical properties.

I. INTRODUCTION

TCOs have been integrated in several fields such as: transistors [1,2], solar cells [3], organic light emitting diodes, and electrochromic windows [4]. Among these oxides zinc oxide ZnO is with the properties optical and electric has attracted the attention of researchers for a long time, its thermal and chemical stability very high, it's no toxicity like its abundance in the nature more. Zinc oxide has found special interest for several applications such as a transparent conducting film for displays and photovoltaic panels [5-6]. LEDs and the inexpensive transistors [7-9] , gas sensing detectors [10], spintronics [11], smart textiles [12,13]. Many methods were employed to produce the ZnO thin films such as magnetron sputtering [14-15], sol–gel, CVD [16], RF sputtering [17], hydrothermal [18], atomic layer epitaxy [19], pulsed laser deposition [20-21], spray pyrolysis [22-23].

The spray pyrolysis used to prepare thin films by directing them to a substrate for depositing thin layers. This technique can prepare large areas of layers for the technological applications despite the simplicity of its equipment, making it important in the industrial vision, and it can prepare high quality layers with the ability to control the thicknesses and quality by the process parameters such as, distance between nozzle orifice and substrate surface, nozzle shape and dimensions, precursor material and concentration, flow rates of gas and solution, spray time and substrate temperature [24-26].

The aim of this work is to study the optical properties of ZnO thin films prepared by spray pyrolysis method under different spray times. Transmittance measurements under UV-Visible. The evolution of the properties of the sprayed ZnO films is discussed and correlated to the deposition conditions.

II. EXPERIMENTAL DETAILS

ZnO thin films were grown onto glass substrate, using a spray pyrolysis technique. A solution of 0.1 morality was prepared by dissolving zinc acetate dihydrate $C_4H_6O_4Zn.2H_2O$ precursor in a methanol CH_4O. The substrates temperature was fixed at 350 ◦C. A set of samples was prepared by varying the deposition time Td in the range of 2 min-8 min to investigate the influence of deposition time on the optical properties of ZnO films.

The optical transmission in the UV–visible range (300–1100 nm) measurements was performed using Shimadzu UV-1601 PC spectrophotometer. Films thicknesses and optical band gaps were estimated from fitting optical transmission data.

III. RESULTS AND DISCUSSION

The optical transmission spectra for as-prepared films with different deposition time are given in Fig. 1 The average optical transmittance values of all the films were higher than 75% in the visible light and near infrared regions. The films' optical transmittances fell off at the UV region with wavelength shorter than 380 nm. In the UV region with wavelength lower than 380 nm, the ZnO film showed the lowest transmittance.

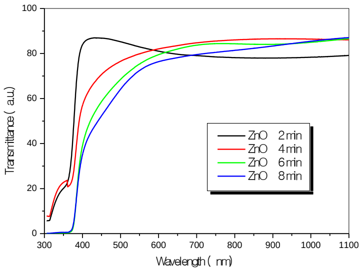

Fig. 1. Spectral variation of transmittance with different deposition time (T_d).

Films optical band gaps are estimated, as shown in Fig. 2 from the plot $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$), according to Tauc formula for direct band gap semiconductors [27]:

$$(\alpha h\nu)^2 = B(Eg - h\nu) \qquad (1)$$

where B is a constant, Eg the band gap energy .

Localized states appears near the bands edges which causes band tails formation due to the disorder in film network. These band tail states are responsible for the photon absorption in the low energies range. In this range the absorption coefficient is given by [28]:

$$(\alpha h\nu) = \alpha_0 \exp(h\nu/E_u) \quad (2)$$

where α_0 is a constant, E_u is disorder energy commonly called Urbach tail [29].

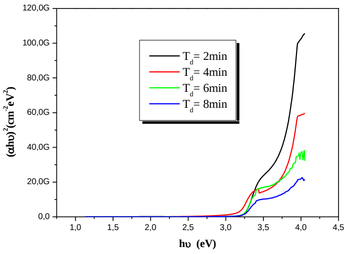

Fig. 2. Typical variation of the quantity $(ah\nu)^2$ as a function of photon energy.

The variations of the calculated band gap and disorder energy with deposition time are reported in Fig. 3.

We note a reduction in the gap with the deposition time. As seen, the variations of both Eg and Eu correlate very well, this indicates that the variation of the optical gap is governed by the disorder in the film. Meyer et al. [30].

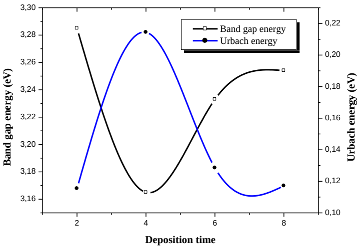

Fig. 3. Variation of the optical gap and Urbach energy as a function of the deposition time.

Authors should discuss the results and how they can be interpreted in perspective of previous studies and of the working hypotheses. The findings and their implications should be discussed in the broadest context possible. Future research directions may also be highlighted.

IV. CONCLUSIONS

In present work, ZnO thin films have been synthesized using spray pyrolysis technique. The influence of deposition time on films properties has been investigated. The obtained results indicate that ZnO films properties are sensitive to the deposition time. The values of the optical band gap and Urbach energy change with deposition time. In the visible region, all the films are highly transparent more than 75%.

REFERENCES

[1] Y. Sun and J. A. Rogers, "Inorganic semiconductors for flexible electronics," Adv. Mater., vol. 19, no. 15, pp. 1897–1916, 2007.

[2] J. H. Kim, B. Du Ahn, C. H. Lee, K. A. Jeon, H. S. Kang, and S. Y. Lee, "Characteristics of transparent ZnO based thin film transistors with amorphous HfO2 gate insulators and Ga doped ZnO electrodes," Thin Solid Films, vol. 516, no. 7, pp. 1529–1532, 2008.

[3] N. Ohashi, K. Kataoka, T. Ohgaki, T. Miyagi, H. Haneda, and K. Morinaga, "Synthesis of zinc oxide varistors with a breakdown voltage of three volts using an intergranular glass phase in the bismuth–boron–oxide system," Appl. Phys. Lett., vol. 83, no. 23, pp. 4857–4859, 2003.

[4] S. J. Jiao et al., "ZnO p-n junction light-emitting diodes fabricated on sapphire substrates," Appl. Phys. Lett., vol. 88, no. 3, p. 31911, 2006.

[5] T. Kogure and Y. Bando, "Formation of ZnO nanocrystals in the cubic phase was reported by electron-beam induced oxidation of ZnS surfaces during TEM observations," J. Electron. Microsc, vol. 47, pp. 7903–7909, 1993.

[6] A. B. M. A. Ashrafi et al., "Growth and characterization of hypothetical zinc-blende ZnO films on GaAs (001) substrates with ZnS buffer layers," Appl. Phys. Lett., vol. 76, no. 5, pp. 550–552, 2000.

[7] P. Kacman, "Spin interactions in diluted magnetic semiconductors and magnetic semiconductor structures," Semicond. Sci. Technol., vol. 16, no. 4, p. R25, 2001.

[8] J. K. Furdyna, "Diluted magnetic semiconductors," J. Appl. Phys., vol. 64, no. 4, pp. R29–R64, 1988.

[9] S. A. Wolf et al., "Spintronics: a spin-based electronics vision for the future," Science (80-.)., vol. 294, no. 5546, pp. 1488–1495, 2001.

[10] H. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, Semiconducting transparent thin films. Institute of Physics Bristol, 1995.

[11] D. P. Norton, S. J. Pearton, A. F. Hebard, N. Theodoropoulou, L. A. Boatner, and R. G. Wilson, "Ferromagnetism in Mn-implanted ZnO: Sn single crystals," Appl. Phys. Lett., vol. 82, no. 2, pp. 239–241, 2003.

[12] Ü. Özgür et al., "A comprehensive review of ZnO materials and devices," J. Appl. Phys., vol. 98, no. 4, p. 11, 2005.

[13] C. Jagadish and S. J. Pearton, Zinc oxide bulk, thin films and nanostructures: processing, properties, and applications. Elsevier, 2011.

[14] P. F. Carcia, R. S. McLean, M. H. Reilly, and G. Nunes Jr, "Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering," Appl. Phys. Lett., vol. 82, no. 7, pp. 1117–1119, 2003.

[15] L.-Y. Chen, W.-H. Chen, J.-J. Wang, F. C.-N. Hong, and Y.-K. Su, "Hydrogen-doped high conductivity ZnO films deposited by radio-frequency magnetron sputtering," Appl. Phys. Lett., vol. 85, no. 23, pp. 5628–5630, 2004.

[16] A. HAFDALLAH, K. DERRAR, M. S. AIDA, and N. ATTAF, "Effet de la solution précurseur sur les propriétés structurales et optiques des couches minces de ZnO préparées par spray pyrolyse," Afrique Sci., vol. 12, no. 3, pp. 26–33, 2016.

[17] H. S. Yoon et al., "Properties of fluorine doped ZnO thin films deposited by magnetron sputtering," Sol. Energy Mater. Sol. Cells, vol. 92, no. 11, pp. 1366–1372, 2008.

[18] T. Sekiguchi, S. Miyashita, K. Obara, T. Shishido, and N. Sakagami, "Hydrothermal growth of ZnO single crystals and their optical characterization," J. Cryst. Growth, vol. 214, pp. 72–76, 2000.

[19] Y.-J. Lee et al., "Efficient hydrogenated amorphous silicon thin-film solar cells using zinc oxide deposited by atomic layer deposition as a protective interfacial layer," J. Phys. Chem. C, vol. 116, no. 44, pp. 23231–23235, 2012.

[20] V. Craciun, J. Elders, J. G. E. Gardeniers, and I. W. Boyd, "Characteristics of high quality ZnO thin films deposited by pulsed laser deposition," Appl. Phys. Lett., vol. 65, no. 23, pp. 2963–2965, 1994.

[21] K. L. Narasimhan, S. P. Pai, V. R. Palkar, and R. Pinto, "High quality zinc oxide films by pulsed laser ablation," Thin Solid Films, vol. 295, no. 1–2, pp. 104–106, 1997.

[22] A. Hafdallah, A. Azzedine, H. Belhani, M. S. Aida, and N. Attaf, "Effect of the Nozzle-Substrate Distance on the Structural and Optical Properties of ZnO Thin Films Deposited by Spray Pyrolysis Technique," Am. J. Nano Res. Appl., vol. 5, no. 6, p. 87, 2017.

[23] M. de la L. Olvera, A. Maldonado, R. Asomoza, M. Konagai, and M. Asomoza, "Growth of textured ZnO: In thin films by chemical spray deposition," Thin Solid Films, vol. 229, no. 2, pp. 196–200, 1993.

[24] V. Vasu and A. Subrahmanyam, “Electrical and optical properties of pyrolytically sprayed SnO2 film—Dependence on substrate temperature and substrate-nozzle distance,” Thin Solid Films, vol. 189, no. 2, pp. 217–225, 1990.

[25] Y. S. Sakhare, N. R. Thakare, and A. U. Ubale, “Influence of quantity of spray solution on the physical properties of spray-deposited nanocrystalline MgSe thin films,” Научно-технические ведомости Санкт-Петербургского государственного политехнического университета. Физико-математические науки, no. 1 (237), 2016.

[26] W. Sripianem et al., “Effect of aluminium doping concentration on microstructures, optical and electrical properties of ZnO thin films by spray pyrolysis technique,” Mater. Today Proc., vol. 5, no. 3, pp. 9519–9524, 2018.

[27] L. A. Goodman, “Liquid-crystal displays—Electro-optic effects and addressing techniques,” in Introduction to Liquid Crystals, Springer, 1975, pp. 241–279.

[28] C. M. Lampert, “Heat mirror coatings for energy conserving windows,” Sol. Energy Mater., vol. 6, no. 1, pp. 1–41, 1981.

[29] J. Tauc, “Optical properties of amorphous semiconductors,” in Amorphous and Liquid Semiconductors, Springer, 1974, pp. 159–220.

[30] F. Urbach, “The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids,” Phys. Rev., vol. 92, no. 5, p. 1324, 1953.