International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/090206

Fabrication and Characterization of Cobalt Pigmented Anodized Zinc for Photocatalytic Application

Judith Chebwogen[1*], *Onesmus Munyati*[2], *Sylvester Hatwaambo*[3], *Mghendi Mwamburi*[4] *and Christopher Maghanga*[1]

[1]Department of Physical & biological Sciences, Kabarak University, P.O Private Bag – 20157 Kabarak, Kenya.
[2]Department of Chemistry, University of Zambia, P. O. Box 32379 Lusaka, Zambia.
[3]Department of Physics, University of Zambia, P. O. Box 32379 Lusaka, Zambia.
[4]Department of Physics, University of Eldoret, P.O. Box 1125- 30100 Eldoret, Kenya.

Received: 21 Feb. 2020, Revised: 22 Mar. 2020, Accepted: 24 Mar. 2020.
Published online: 1 May 2020.

Abstract: ZnO is an n-type oxide semiconductor with a direct wide band gap greater than 3 eV. Like any other semiconductor, the optical and electrical characteristics can be influenced by doping or adjusting process conditions which broaden its applications. In this work, varying amounts of Cobalt (0.01g-0.04g) were electrodeposited on anodized Zinc thin films (ZnO) followed by heat treatment to about 250^0C. Optical characterization was performed in the range 300-2500 nm to obtain reflectance data which aided in defining the absorption coefficient and band gap of the films. Photocatalytic activity of the films was explored in Methylene Blue solution degradation under UV light irradiation. Analyzed data revealed a band gap shift to the red, i.e. from 3.34 eV to 3.10 eV for pure ZnO and 0.04g-Cobalt pigmented ZnO thin films respectively. Moreover, absorption coefficient increased with pigmentation attributed to the band shrinkage effect which elucidates that ZnO:Co thin films serve as good candidates for application in photocatalysis. All the fabricated films were photocatalytic but ZnO thin films containing 0.02g of Cobalt was the most photocatalytic.

Keywords: Anodization, ZnO, band gap, optical characterization, photocatalysis, pigmentation

1 Introduction

ZnO has diverse applications because many relevant researches were conducted [1]. It is a direct band gap semiconductor whose band gap ranges from 3.2 to 3.37eV. It also has found applications in light emitting diodes [2,3], gas sensing[4], Acoustic Sensors [5], Piezo-Phototronics [6,7]. Some of the earlier work addressed anodized or electrodeposited Cobalt doped ZnO thin films dwelt on ferromagnetism [8] and field emission characteristics [9], but an investigation on their possibility to be used in photocatalysis has not been reported. Although nanoparticles and nanorods are some of the prefered choices for photocatalysis, thin films are recyclable and their reusability also allows for their application in photocatalysis. ZnO photosensitivity, non-toxicity and environmental stability make it a promising photocatalyst. However, it has a wide band gap which makes it absorb a narrow range of the solar spectrum. Altering its bandgap edge towards the visible range is likely to boost its photocatalytic properties. This can be achieved by semiconductor coupling or doping with a transition metal or non-metal [10,11]. Bahsi and Oral [12] demonstrated that doping ZnO with a transition metal is the most effective because it reduces its band gap, expanding its response to light from the UV to the visible range. Theoretically, for the purpose of photocatalysis, Cobalt is among the preferred dopants of ZnO since it has an ionic radius of 0.745 Å which is almost similar to that of Zinc (0.74 Å) [13], and so can substitute the Zn ions in the ZnO crystal lattice. Given that the band gap is among the key determinants of the physical properties of a semiconductor, it is important to note that doping ZnO with a transition metal may lead to either band gap widening (BGW) or band gap narrowing (BGN) [14]. BGN is a consequence of several body effects on the conduction and the valence bands while BGW arises from Burstein–Moss effect [15,16]. Several authors have addressed the two concepts (BGN and BGW). Jain *et al* [14] represented the decrease in band gap as follows:

*Corresponding author E-mail: judithkoskey86@gmail.com

$$\Delta E_g = \Delta E_{ex(maj)} + \Delta E_{cor(mino)} + \Delta E_{int(maj)} + \Delta E_{int(mino)} \quad (1)$$

where, the four terms respectively signify shift of the majority band edge due to exchange energy, correlation energy shift of the minority band edge, and carrier-impurity interaction shifts of the two band edges. The details of this equation can be found in reference [14].

ZnO has been synthesized using different techniques such as sol gel, spray pyrolysis, sputtering, hydrothermal and co-precipitation methods but anodization is an easy low cost route in the synthesis of thin films [17] and the method has been succesfully employed by several researchers to deposit ZnO thin films[18,19,20]. In this paper, we report the optical properties of Cobalt pigmented anodized Zn and its photocatalytic activity.

2 Experimental Section

2.1 Preparation of ZnO thin films

ZnO thin films were prepared by anodizing a polished ultrasonicated Zinc metal in 0.5M magnetically stirred Oxalic acid. The experiment was performed at room temperature at a constant voltage of 10V using zinc plate working electrode and graphite plate as the counter electrode for 60 minutes. The set up for anodization is shown in figure 1.

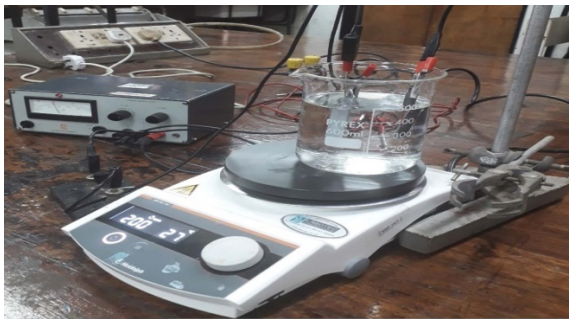

Figure 1. Experimental setup for anodization of the Zinc plates.

Varying amounts of Cobalt ranging from 0.01g to 0.04g were electrodeposited onto the ZnO thin films by increasing the deposition time from 10s, 20s, 40s and 60s. Cobaltous sulphate was used as the source of Cobalt, ZnO the working electrode and graphite the counter electrode and 2.18 A current passed at a constant voltage of 20V. Then, the films were rinsed and left to dry then heated to about 250^0C for 2 hours in a furnace. The amount (mass in grams) of Cobalt in the ZnO films was obtained using the Faraday's law of electrochemistry expressed as [21]:

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right) \quad (2)$$

Where Q expressed as Q=It is the charge passed through the substance in coulombs, F is the Faraday constant (96485.33289 $Cmol^{-1}$), M is the molar mass of the substance in grams mol^{-1} and z is the valence number of the substance. In this case the substance is Cobalt.

2.2 Characterization of ZnO thin films

Optical characterization of the prepared ZnO films was performed in the range 300nm to 2500nm using UV/VIS/NIR Perkin Elmer Lambda 19 spectrophotometer where reflectance data was obtained and aided in the determination of the absorption coefficient and optical band gap of the films. This was done by fitting the measured reflectance spectra onto the simulated spectra in the SCOUT software. The Drude, Harmonic and Tauc Lorentz models in the software enabled the fitting of the spectra and so the film thickness which was read directly once a perfect fit was obtained. The average film thickness obtained was 110nm. Figure 2 illustrates the fitting done using the SCOUT software.

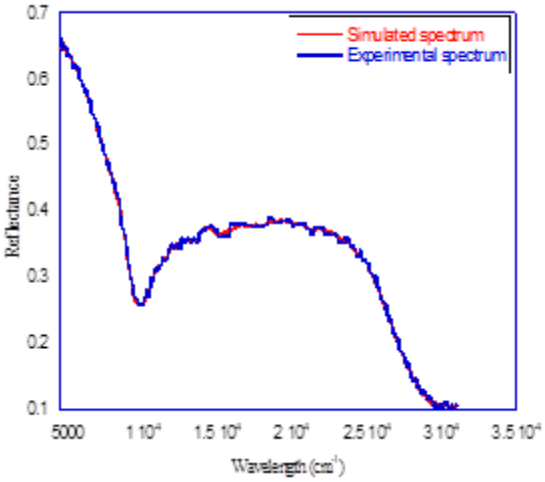

Figure 2. An illustration of fitting of the experimental to simulated spectra using the SCOUT software.

2.3 Photocatalytic experiments

The photocatalytic activities of the films in the degradation of 10ppm methylene blue solution was investigated under UV light irradiation in a UV cabinet with a UV lamp of wavelength 366nm, 2×6W irradiation power and an Optima SP-3000nano UV-VIS spectrophotometer. 60ml Methylene blue solution was first placed in the dark for 60 minutes for absorption-desorption balance to be attained then transferred into the cabinet and irradiated for 300 minutes. 1ml of the degrading solution was drawn at intervals of 30 minutes and the absorbance at 664nm measured using the spectrophotometer. The concentration was obtained using calibration curve from standard methylene blue solutions prepared prior to the experiment.

3 Results and Discussion

3.1 Formation of the ZnO films

ZnO films were successfully fabricated, led to the formation of a whitish film of thickness of about 110 nm on the Zinc substrate. The whitish film resulted from passing of a constant current from the power supply across the zinc metal and graphite electrodes. Consequently, redox reactions led to the formation of the oxide where $Zn(OH)_2$ formed on the Zinc metal surface further dissociating to ZnO as summarized by the equations below:
At the graphite plate (counter electrode)

$$2H^+ + 2e^- \rightarrow H_2\ (g) \quad (3)$$

At the Zinc plate (working electrode):

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (4)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (5)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (6)$$

The films were labeled ZnO, ZnO:Co0.01, ZnO:Co0.02, ZnO:Co0.03, and ZnO:Co0.04 with respect to the Cobalt content in the fims. The ZnO films began to darken when Cobalt was introduced and darkening increased as the mass of Cobalt in the films increased as shown in figure 3.

ZnO ZnO:Co0.01 ZnO:Co0.02 ZnO:Co0.03 ZnO:Co0.04

Figure 3. A photo of the fabricated films.

The darkening of the films was attributed to the presence of Cobalt which increased as the Cobalt content in ZnO thin films increased and might have improved films absorption.

3.2 Reflectance and absorption of the fabricated films

Figure 4 shows the reflectance spectra for all the prepared films obtained from the spectrophotometer.

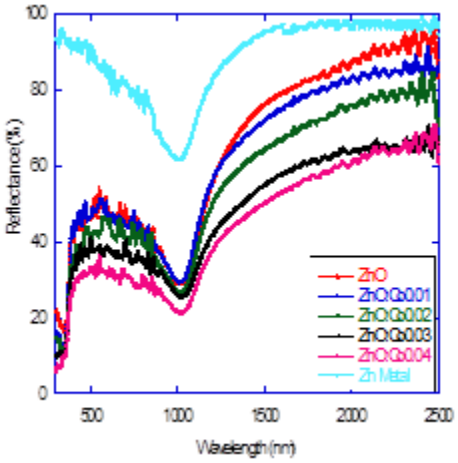

Figure 4. Measured reflectance for polished Zinc metal and the ZnO films with varying masses of Cobalt.

Reflectance of polished Zinc metal is higher than 60% before anodization because of its shiny nature. ZnO films have a relatively lower reflectance compared to that of Zinc metal. A sharp decrease in the ZnO reflectance spectra was observed at about 348nm which corresponds to its absorption edge. All the spectra had a depth at about 1100nm due to Interband transitions arising from the zinc substrate.

As the Cobalt content increased, a decrease in reflectance was observed showing an increase in absorbance. The decrease was attributed to the darkening of the ZnO films as the Cobalt content increased as shown in Figure 3. This is supported by absorption coefficient data for the films. Given that they were deposited on opaque substrates where T = 0, α was estimated using the rough approximation [22]:

$$R + T = e^{-\alpha d} \quad (7)$$

Which yields;

$$\alpha = \frac{1}{d} In\left(\frac{1}{R}\right) \quad (8)$$

The graph obtained using equation 8 is as shown in figure 5.

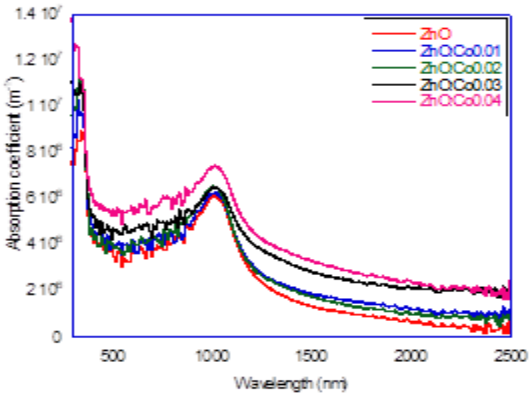

Figure 5. Absorption coefficient as a function of wavelength

Figure (5) reveals that the sudden increase in the absorption coefficient at about 348nm corresponds to the absorption edge while peak at about 1100 nm occurs due to Zn substrate. There is also a systematic increase in absorption coefficient with increase in pigmentation which can be attributed to increase carrier absorption. However, Figure 4 exhibits that reflectance decreased with increased pigmenting. Films roughness may increase with pigmentation which leads to optical losses in form of scattering [23] which explains the increase in the absorption coefficient.

3.3 Optical Band Gap

The optical band gap of the films was defined using the Tauc's plot of $(\alpha h\nu)^2$ against $h\nu$. Figure 6 reveals the obtained band gaps for the films.

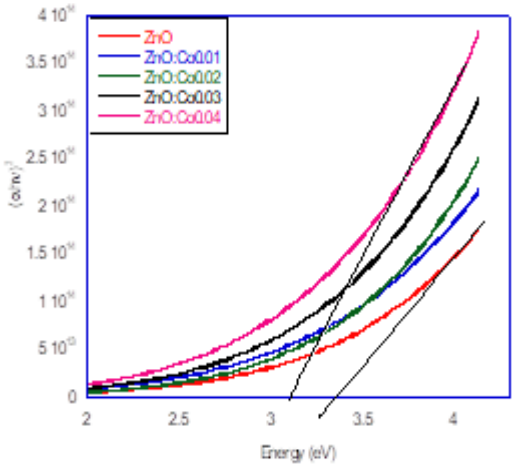

Figure 6. Graph showing the optical band gaps of the fabricated films.

The optical band gaps of the films ranged from 3.34 eV to 3.10 eV. The fabricated pure ZnO films had a band gap of 3.34 eV which is similar to the previous work conducted by Yildirim *et al* [24] and Kalphe *et al* [25]. In both cases, a gradual BGN was observed in the films with increase in the Cobalt content which agrees with our work. This BGN as discussed in equation 2 may have resulted from a shift of the majority band edge due to exchange energy, correlation energy shift of the minority band edge, and carrier-impurity interaction shifts of the two band edges.

3.4 Photocatalytic activity of the films

The radiation assisted methylene blue degradation follows the pseudo first order kinetics [26] which involves presentation of raw data as integral data. The photocatalytic activity of the films obtained is presented in figure 7.

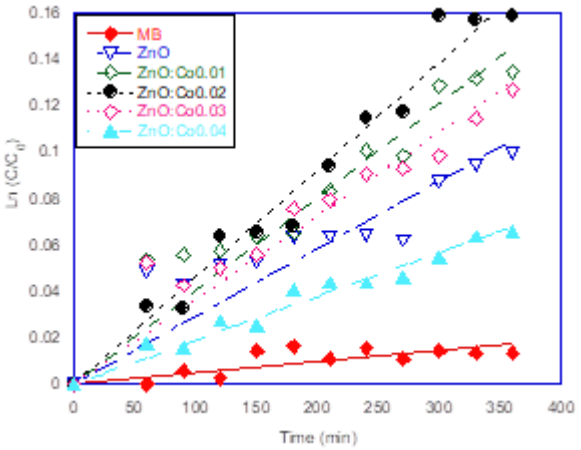

Figure 7. A graph of ln (C/C_0) versus time in minutes

As observed in the figure, the rate at which methylene blue with catalyst degraded was faster than that without the catalyst. Also, Cobalt pigmenting increased the degradation rate which may be attributed to the reduction in the optical band gap resulting from the red shift in the reflectance spectra which allowed more electrons to gain kinetic energy and move to the conduction band and take part in the degradation process. Cobalt pigmenting also increased the absorption coefficient implying that more radiation was absorbed and so excited more electrons to the conduction band.

However, heavy Cobalt pigmenting lowered the methylene blue degradation rate. This may be due to the fact that excess metal pigment covered the active sites of the *ZnO* catalyst lowering its activity or the generation of the impurity levels deep in *ZnO* band gap which acted as centers for recombination for the photogenerated electrons.

4 Conclusion

In this paper, ZnO was successfully fabricated by anodization. The color of the film formed was white. Reflectance of the ZnO films decreased with increase in Cobalt content deposited. Consequently, films roughness that increased with increase in Cobalt content raised pigmentation and absorption. The band gap of ZnO changed from 3.34 eV for unpigmented to 3.10 eV for the most pigmented film. The decrease in reflectance and band gap shrinkage or narrowing indicates an increase in the solar absorption which is one of the most important factors defining semiconductor photocatalysis. All the films were photocatalytic but ZnO thin films with 0.02g of Cobalt was the most photocatalytic.

Acknowledgement

The author (Judith) is grateful to the International Science Programme of Uppsala University, Sweden for the direct financial support and the University of Zambia where experimental work was done.

References

[1] Özgür, Ü., Alivov, Y. I., Liu, C., Teke, A., Reshchikov, M., Doğan, S., & Morkoç, H.. A comprehensive review of ZnO materials and devices*, J. Appl. Phys*., **98(4)**, 11 (2005).

[2] Bacaksiz, E.; Parlak, M.; Tomakin, M.; Özcelik, A.; Karakiz, M.; Altunbas, M. The effect of zinc nitrate, zinc acetate and zinc chloride precursors on investigation of structural and optical properties of ZnO thin films. *J. Alloy. Compd*., **466**, 447–450(2008).

[3] Kołodziejczak-Radzimska, A., & Jesionowski, T. Zinc oxide—from synthesis to application*: a review. Materials*., **7(4)**, 2833-2881(2014).

[4] Galstyan, V., Comini, E., Baratto, C., Faglia, G., & Sberveglieri, G. Nanostructured ZnO chemical gas sensors*. Ceram. Int.,* **41(10)**, 14239-14244(2015).

[5] Suma, M. N., Prasad, M. V. N., Gaddam, V., Rajanna, K., & Nayak, M. M. Development of a Novel Acoustic Sensor using Sputtered ZnO Thin Film. *J. Pure Applied. Ind. Phys*, **9(1)**, 1-7(2019).

[6] Zhu, L., & Wang, Z. L. Recent Progress in Piezo-Phototronic Effect Enhanced Solar Cells*. Adv. Funct. Mater.,* **29(41)**,1808214, (2018).

[7] Wang, J.; Cao, J.; Fang, B.; Lu, P.; Deng, S.; Wang, H. Synthesis and characterization of multipod, flower-like, and shuttle-like ZnO frameworks in ionic liquids. *Mater. Lett*., **59(11)**, 1405–1408(2005).

[8] Wang, A., Zhong, Z., Lu, C., Lv, L., Wang, X., & Zhang, B. Study on field-emission characteristics of electrodeposited Co-doped ZnO thin films. *Physica B: Condensed Matter*., **406(5)**, 1049-1052(2011).

[9] Simimol, A., Anappara, A. A., Greulich-Weber, S., Chowdhury, P., & Barshilia, H. C. Enhanced room temperature ferromagnetism in electrodeposited Co-doped ZnO nanostructured thin films by controlling the oxygen vacancy defects*. Journal of Applied Physics*., **117(21)**, 214310(2015).

[10] Gupta, R., Eswar, N. K., Modak, J. M., & Madras, G. Ag and CuO impregnated on Fe doped ZnO for bacterial inactivation under visible light. *Catal. Today*., **300**, 71-80(2018).

[11] Malik, G., Mourya, S., Jaiswal, J., & Chandra, R. Effect of annealing parameters on optoelectronic properties of highly ordered ZnO thin films. *Mat. Sci. Semicon. Proc*., **100**, 200-213(2019).

[12] Bahşi, Z. B., & Oral, A. Y. Effects of Mn and Cu doping on the microstructures and optical properties of sol–gel derived ZnO thin films. *Opt. Mater*., **29(6)**, 672-678(2007).

[13] Woo, H. S., Kwak, C. H., Chung, J. H., & Lee, J. H. Co-doped branched ZnO nanowires for ultraselective and sensitive detection of xylene. *ACS Appl. Mater. Inter*., **6(24)**, 22553-22560(2014).

[14] Jain, A., Sagar, P., & Mehra, R. M. Band gap widening and narrowing in moderately and heavily doped n-ZnO films. *Solid. State. Electron*., **50(7-8)**, 1420-1424(2006).

[15] John C. Inkson, *Many-Body Theory of Solids: An Introduction Plenum*, New York.,5-17, (1984).

[16] Sernelius, B. E., Berggren, K. F., Jin, Z. C., Hamberg, I., & Granqvist, C. G. Band-gap tailoring of ZnO by means of heavy Al doping. *Phys. Rev. B*., **37(17)**, 10244(1988).

[17] Chuah, L. S., Hassan, Z., & Bakhori, S. M. (2012). *Nanoporous ZnO prepared by electrochemical anodization deposition*. In Third International Conference on Smart Materials and Nanotechnology in Engineering. International Society for Optics and Photonics. Vol. 8409, p. 84092E(2012)

[18] Yamaguchi, Y., Yamazaki, M., Yoshihara, S., & Shirakashi, T. Photocatalytic ZnO films prepared by anodizing*. J. Electroanal. Chem*., **442(1-2)**, 1-3(1998).

[19] Basu, P. K., Saha, N., Maji, S., Saha, H., & Basu, S. Nanoporous ZnO thin films deposited by electrochemical anodization: effect of UV light*. J. Mater. Sci.: Mater. Electron*., **19(6)**, 493-499(2008).

[20] Voon, C. H., Derman, M. N., Hashim, U., Lim, B. Y., Sam, S. T., Foo, K. L., & Ten, S. T. Synthesis of nanoporous zinc oxide by anodizing of zinc in distilled water. *Appl. Mech. Mater*., **754**, 1126(2015).

[21] Bhattacharyya, B. "*Electrochemical micromachining for nanofabrication.*" MEMS and Nanotechnology, William Andrew Applied Science Publishers, Imprint of Elsevier Inc., Massachusetts ., 270(2015).

[22] Kushagra, A., & Pandey, A. K. S. H. A. Y. A. Generation of near-UV Absorption Band at Extremely Alkaline pH in Colloidal Coffee. *Orient. J. Chem*., Vol. **36(1),** 201-205 (2020)

[23] Babeva, T., Todorov, R., Mintova, S., Yovcheva, T., Naydenova, I., & Toal, V. Optical properties of silica MFI doped acrylamide-based photopolymer. J. Opt. A-Pure. Appl. Op., 11(2), 024015(2009).

[24] Yildirim, O. A., Arslan, H., & Sönmezoğlu, S. Facile synthesis of cobalt-doped zinc oxide thin films for highly

efficient visible light photocatalysts. *Appl. Surf. Sci*., **390**, 111-121(2016).

[25] Kaphle, A., Reed, T., Apblett, A., & Hari, P. Doping Efficiency in Cobalt-Doped ZnO Nanostructured Materials. *J. Nanomater*. 2019 https://doi.org/10.1155/2019/7034620., (2019).

[26] Gajbhiye, S. B. Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent. *Int. J. Mod. Eng. Res*., **2(3)**, 1204-1208(2012).