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Electrodeposition of Binary ZnO-MgO Nanocomposite Thin Films: Influence of pH Bath on Microstructural and Optical Properties

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Abstract

The article examines the influence of pH bath on microstructure and optical properties of nanocomposite thin films of ZnO-MgO films. These films were fabricated through potentiostatic electrodeposition on fluorine-doped tin oxide (FTO) coated glass substrates, utilizing a mixed electrolyte solution containing 40 mM (40%) $Zn(NO_3)_2 \cdot 6H_2O$ and 40 mM (60%) $Mg(NO_3)_2 \cdot 6H_2O$. The resulting ZnO-MgO nanocomposites were characterized using optical spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD) to analyze their structural and optical features. It was found that bath pH makes a large difference in the surface morphology, microstructural and optical characteristics. It shows that the thickness of the films increases between 341 - 451 nm and crystallite size of the film is reduced between 12.561 - 12.034 nm with pH value of 4.0, 5.0 and 6.0. The optical conductivity rose to 7.250 x10^{11} - 11.449 x10^{11} $^{-1}$ $\Omega^{-1}m^{-1}$ and the refractive index rose from 1.859 to 2.226, whereas the band gap and transmittance decreased from 3.28- 3.12 eV and 81- 56% respectively when the bath pH values rose.

Keyword: *Zinc Oxide, Magnesium Oxide, Nanocomposite, Optical Properties, Microstructural Properties, Electrodeposition and Optoelectronics.*

I. INTRODUCTION

The metal-oxide Nanocomposite thin films have remained in use in the electronics and optoelectronics due to its high infrared reflections, huge transmittance in the visible region, high optical conductivity, reduced resistivity, and broad band gap energy. ZnO and MgO have now turned out to be the great transparent conductive oxide due to their improved optical and microstructural characteristics which make them effective transparent electrodes in various devices such as flat panel displays, solar cells, thin film transistors, and biochemical sensor (Alias *et al.* 2010, Othmen *et al.*, 2018). The types of metal-oxide nanocomposites thin films especially ZnO-MgO have shown certain chemical and physical attributes that have been applied in extensive applications optical devices, chemical and biosensors (Guichaoua *et al.* 2016; Bandyopdhay *et al.* 2020; Egwunyenga *et al.* 2019). ZnO-MgO in form of a single nanocomposite is said to enhance the optical properties besides increasing the band gap energy due to the electronic interaction between ZnO and MgO (Islam *et al.* 20019; Ahmad *et al.* 2010). There are several of deposition methods that have been reported to make ZnO-MgO nanocomposite thin films. The other deposition methods have been established as electrodeposition which has been found to be the most useful due to low operating temperatures, thickness of the film can be controlled, low complexity of operation, low equipment maintenance and would easily process large area thin films. Several studies have explored the property of the nanocomposite thin films of ZnO-MgO. Egwunyenga *et al.* (2019) investigated how the annealing temperature influenced the optical properties of electrodeposited ZnO-MgO super lattices and they found out that the annealing temperature played a critical role in enhancing the optical performance. It was found that band gap reduced with rise in temperature of annealing 523 K-673 K as well as the thickness of the film was increased with increase in annealing temperature. Optical conductivity on the other hand declined as annealing temperature increased. Similarly, Bandyopadhyay *et al.* (2020) investigated the microstructural and optical characteristics of ZnO/MgO nanocomposite thin films reported the energy of the band gaps had reduced to 2.98 eV, and with 75 Zn-25 Mg compositions. Moreover, Abed *et al.* (2020) examined the ZnO/MgO thin films that were made by sputtering in order to arrive at the conclusion that the optical properties of the films would vary depending on various concentrations of Mg (1 wt% 2 wt% 5 wt%, and 10 wt%). The study showed that the most crystalline films were the ones with 2 wt% MgO and those with the best optical characteristics. The article examines the electrodeposition of binary ZnO-MgO nanocomposite thin films and how pH bath values influence the films' microstructural and optical properties.

II. MATERIALS AND METHOD

The nano-compositions and thin films of ZnO-MgO were electrodeposited potentiostatically on the FTO-covered with glass substrate through a bath solution containing 40 mM (40%) of Zinc nitrate hexahydrate and 40mM (60%) of magnesium nitrate hexahydrate. It was washed by ultrasonic method with acetone then the FTO substrate was deposited. Zinc nitrate hexahydrate 40mM concentration was made individually by dissolving 3.0 g in 250 ml of deionized water in 300 ml beaker. Also magnesium nitrate hexahydrate 40 mM concentration was made independently by dissolving 2.6 g of magnesium nitrate hexahydrate in 250 ml of deionized water in 300 ml beaker. The ZnO-MgO solution mixture was then prepared by mixing 40% of 40 mM $Zn\,(NO_3)_2.6\,H\,2O$, and 60% of 40 mM $Mg\,(NO_3)_2.6\,H\,2O$. The solution was stirred by 2hrs with the help of a magnetic stirrer. NaOH and Hcl was used to adjust the pH of the bath to 4.0, 5.0 and 6.0. The electrodeposition was done using a Metrohm AUTOLAB PGSTAT302N system set-up of three electrodes (FTO) in the electrodeposition where the working (WE), counter (CE) and reference electrode (RE) were placed as FTO, platinum plate wires, and Ag/AgCl respectively. Teflon tape was used to hold the electrodes in the cell, in the vertical position. This was accomplished by the ZnO-MgO nano-composite thin films, which were electrodeposited at 80^{o}C bath temperature and -1.12 V of the cathodic potential at three different pH of 4.0, 5.0 and 6.0. The films were washed in deionized water after every deposition to wash off those that were loosely attached, dried at 200^{o}C in the oven and annealed at 500^{o}C with a period of 2hr. An X-ray diffractometer and a UV-Vis spectrophotometer were employed to analyze the structural morphology and optical characteristics, respectively, of the annealed ZnO-MgO nanocomposite thin films produced through electrodeposition.

The thickness (t) of ZnO-MgO thin films electrodeposited was estimated and determined by the gravimetric technique provided by Kumar, *et al.,* (2019): Ahmed *et al.,* (2019) as equation 1.

$$T = \frac{\Delta m}{\rho A} \tag{1}$$

where Δm represents the average mass of the deposited ZnO-MgO thin film, ρ denotes the density of bulk ZnO, and A also signifies the surface area of the deposited film.

The equation 2 assisted in calculating the size of crystallite of deposited ZnO-MgO thin films using the scherrer formula.

$$D = \frac{K\lambda}{\beta cos\theta} \tag{2}$$

D being the size of crystallites (in nanometers), K the shape factor or constant of Scherrer (K = 0.9), l the wavelength of the X-ray radiation (l = 1.5418 A), b the full width at half maximum (FWHM), and th the Bragg angle.

The dislocation density of the electrodeposited thin film was calculated using equation 3.

$$\delta = \frac{1}{D^2} \tag{3}$$

where δ is the dislocation density, D is crystallite size.

The micro-stain of the electro-deposited thin film was calculated using equation 4

$$E = \frac{\beta}{4\tan\theta} \tag{4}$$

where εis the micro-strain of the deposited thin film, β is FWHM, and θ is the Bragging angle.

The absorption coefficient is given as

$$A = \frac{2.303A}{t} \tag{5}$$

where A absorbance, t is thickness of the film and The optical conductivity (σ)was calculated using equation 6

$$\sigma = \frac{\alpha nc}{4\Pi} \tag{6}$$

Here, α denotes the absorption coefficient, n represents the refractive index, and c is the speed of light.

The band gap energy (E_g) is estimated from the Tauc plots of $(\alpha hv)^2$versus photon energy(hv)

$$(\alpha hv) = A\,(hv - E_g)^{1/2} \tag{7}$$

where A= 1/2 is the constant n =2 is the constant of allowed transition n =3 is the constant of forbidden transition and n =3/2 is the constant of forbidden transition.

Londhe and Chaure, 2017 reported equation 8 used to calculate the refractive index (n) of the deposited ZnO/MgO.

$$N = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \tag{8}$$

where R is the reflectance of the film, n is the refractive index.

III. RESULTS AND DISCUSSION

- *Cyclic Voltammograms*

Electrochemical behaviour of zinc oxide and magnesium oxide was explored in order to identify the appropriate area of growth potential in the electrodeposited of ZnO-MgO. The average of the cyclic voltammogram of the mixture of 40 mM (40%) Zinc nitrate and 40 mM (60%) magnesium nitrate electrolytes at various pH bath values of 4, 5 and 6 of 30 mVs^{-1} scanning rate as presented in Figure 1. The findings indicate that the cathodic potential of the electrodeposition of ZnO-MgO thin film were -1.10 V, -1.09 V and -1.12 V, respectively. The different bath pH values of ZnO-MgO thin films indicated the fact that the thin films that were deposited at - 1.12 V performed better compared to the other thin films as depicted in Figure 1.

- *XRD Analysis*

Figure 2 presents the XRD patterns of ZnO/MgO nanocomposite thin films with varying bath pH. The XRD spectrum showed crystal peaks of ZnO with a Miller index of 100, 002 and 101 of 31.560, 34.210 and 36.510 and crystal peaks of MgO at 220 and 222 (62.35 and 78.60 respectively). The (002) plane reflected in the XRD represents the most intense peak with small broadness suggesting that it has good crystallite and large grain size. The (002) plane with respect to all values of bath pH has an almost same intensity, but diffraction peaks were observed to progress at higher angles with increasing bath pH, indicating a reduction in the crystallite size of the deposited films. The values of the average crystallite sizes in different bath pH values were arrived at. Table 2 indicates that the mean crystallites sizes of the film are lower at a higher pH of the bath. This may be due to the fact that the diffraction peaks shift towards higher angles leading to an increment in stress/strain. The results showed that the thickness of the electrodeposited thin films are relatively large with ZnO/MgO nano-compositions nano-thin films deposited at bath pH of 4. 0 and 6.0 being in the range of 341nm to 451nm. This is in agreement with the results of Egwunyenga *et al.* (2019).

- *Surface Morphology Analysis*

This is shown in Figure 3 that the Scanning Electron Microscopy of the nano-composite of the ZnO -MgO thin films that were electrodeposited using 4.0, 5.0 and 6.0 values of pH were the images formed. The SEM outcome indicates that the pH of the bath is a critical parameter that determine the shape of the films. The photographs are characterized by smooth layers and grains that are pressed against one another. The thin films of ZnO/MgO that were formed in the low pH (4.0) of the bath were densely packed with a smooth surface having a cauliflower-like structure. This structure may be explained by the deposition process by diffusion described earlier by Egwunyenga *et al.* (2019). The thin films deposited at higher bath pH values of 5.0 and 6.0 are aggregates of the smaller grains that were are compacted. The films portray the hard surfaces which are nodular and full of cracks or porous. The films were found to have an increase in the number of pores with progress in the bath pH values. The trends in the obtained results showed that electrodeposited ZnO/MgO thin films morphological characteristics are highly dependent on the bath pH.

- *Optical Properties*

Figure 4 presents the optical transmittance spectra of ZnO-MgO nanocomposite thin films prepared through electrodeposition. The films were electroplated at a cathodic potential of –1.12 V, with the bath pH values varied at 4.0, 5.0, and 6.0 to study their influence on the transmission spectral. The sample at a bath pH of 4.0 have the highest transmittance of 81.6% and hence the lowest transmittance at a bath pH of 6.0 which is 56.2%. Table 2 presents the obtained average structural properties including crystallite size, dislocation density, micro-strain, and thickness of ZnO-MgO thin films prepared at various pH values of the bath. The findings affirmed that the bath pH had a significant effect on the optical quality of the films, as the maximum transparency was found at 4.0 pH and the minimum was found at 6.0 pH. Figure 5 is the absorption coefficient of ZnO/MgO nanocomposite thin films electrodeposited at various bath pH. The findings imply that the change in the absorption coefficient to shorter wavelengths can give reason to believe that the band gap is smaller at higher pH in the bath. MgO might have been present, which may have been a contribution to the decrease in the band gap in the study. Figure 6 presents the dependence of $(ahn)^2$ on Photon energy (hn) of ZnO/MgO nano-composite thin films electrodeposited at varying pH levels of the bath. Band gaps in the three bath pH values of 4.0, 5.0, and 6.0 are 3.28 eV, 3.26 eV and 3.12 eV respectively. The pH value deposited (6.0) has the lowest value of energy band gap (Eg = 3.12 eV). Figure 7 shows the dependence of real part of the refractive index on wavelength. The outcome indicates normal dispersion nature since the refractive index of the electrodeposited ZnO-MgO nanocomposite thin films reduce with the increase in wavelength of the electrodeposited thin films at varying bath pH values. Table 3 indicates that, the higher the cause of the bath pH the higher the refractive index and the thickness of the film. The movies deposited on the bath pH of 6.0 displays the optimum index of refraction. This observation agrees with the results reported by Salim et al. (2017) and Xu et al. (2006). As illustrated in Figure 8, the optical conductivity of the samples deposited at varying bath pH levels decreases with increasing wavelength but rises as the bath pH increases.

IV. CONCLUSIONS

Cathodic electrodeposition has been highly accomplished in the growth of ZnO-MgO nanocomposite thin film on FTO coated glass substrates of various pH value of the bath (4.0, 5.0 and 6.0). The microstructural and optical characteristics of the electrodeposited ZnO/MgO thin films were explored as a result of the bath pH. The findings indicated that bath pH is an important factor in surface morphological and optical characteristics of the electrodeposited thin layers. The ZnO-MgO films that were prepared at the bath pH 4.0 exhibited a uniform structure that was formed with hexagonal grains free of pores and voids, big crystallites size, and least dislocation density, and micro-strain. Sample of high porosity morphology was observed to have high porosity at bath pH of 5.0 and 6.0; and the number of pores grew with the bath pH. When it comes to optical properties, the ZnO-MgO films that have been grown at bath pH of 4.0 demonstrate the best transmittance, lowest refractive index, optical conductivity and high band gap energy. The samples recorded at an increased pH of the bath were more conductive optically and possessed a higher index of refraction. Electrodeposited at bath pH= 6.0 provided the best minimum transmittance, smallest band gap, highest optical conductivity, refractive index, and thickness of the film. These characteristics demonstrate that pH bath conditions play a major role in the microstructure and optical characteristics of electrodeposited ZnO/mgO thin films, and can increase their future use in optoelectronic devices.

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REFERENCES

[1]. Abed, C., Fernández, S. and Elhouichet, H. (2020) Optik Studies of optical properties of ZnO: MgO thin films fabricated by sputtering from homemade stable oversize targets', Optik. *International Journal for Light and Electron Optics. Elsevier, 216164934.*

[2]. Ahmed, N. A., Fortas, G., Hammache, H., Sam, S., Keffous, A., Manseri, A., and Gabouze, N. (2010). Structural and morphological study of ZnO thin films electrodeposited on n-type silicon. *Applied surface science*, *256*(24), 7442-7445.

[3]. Alias, S.S., Ismail, A. B. and Mohamad, A. A. (2010) Effect of pH on ZnOnanoparticle properties synthesized by sol–gel centrifugation, *Journal of Alloys Compound 499 231–237.*

[4]. Bandyopadhyay, N., Gupta, M., Nath, S., Chakraborty, and Sutradhar, S (2020) Magnetic properties of Mn doped ZnO: A Monte Carlo simulation*analysis Vacuum, (183), 109786, 2021*

[5]. Egwunyenga, N. J., Ezenwaka, L. N., Ezenwa, I. A., and Okoli, N. L. (2019). Effect of annealing temperature on the optical properties of electrodeposited ZnO/MgO superlattice. *Materials Research Express*, *6*(10), 105921.

[6]. Guichaoua D., Zawadzka, A., Korcala, J., Strzelecki, P.,Trzaska, and B. Sahraoui (2016) Opiical properties of MgO thin filmgrown *by laser ablation technique pp (1-12).*

[7]. Islam, M. R., Rahman, M., Farhad, S. F. U., and Podder, J. (2019). Structural, optical and photocatalysis properties of sol–gel deposited Al-doped ZnO thin films. *Surfaces and Interfaces*, (*16)*, 120-126.

[8]. Kumar, S., Jeon, H. C., Kang, T. W., Seth, R., Panwar, S., Shinde, S. K. Waghmode, D. P. Saratale,G. S. andChoubey, R.K. (2019) Variation in chemical bath pH and the corresponding precursor concentration for optimizing the optical, structural and morphological properties of ZnO thin films. *Journal of Materials Science: Materials in Electronics, (30), 17747–2789*

[9]. Londhe, P. and Chaure, N. (2017) Effect of pH on the properties of electrochemically prepared ZnO thin films', Materials Science in Semiconductor Processing. *Elsevier, (60) doi: 10.1016/j.mssp.12.005.*

[10]. Muslih, E. Y. and Kim, K. H. (2017) Preparation of Zinc Oxide (ZnO) Thin Film as Transparent Conductive Oxide (TCO) from Zinc ComplexCompound on Thin Film Solar Cells: *Conference Series: Materials Science and Engineering, 214(1).*

[11]. Othmen. B. H., Haned, Z. B., Sieber, B., Addad, A., Elhouichet, H., Boukherroub, R. (2018) Structural and Optical characterization of p-type highly Fe-doped SnO2 thin films and tunnelling transport on SnO2: Fe/p-Si heterojunction, *Applied Surf. Science (434) 879-890.11.019*

[12]. Rahal, H., Kihal, R., Affoune, A. M., Ghers, M., andDjazi, F. (2017). Electrodeposition and characterization of ZnO thin films using sodium thiosulfate as an additive for photovoltaic solar cells. *Journal of Semiconductors*, *38*(5), 053002.

[13]. Ramirez, D., Silva, D., Gomez, H., Riveros, G., Marotti, R. E., and Dalchiele, E. A. (2007). Electrodeposition of ZnO thin films by using molecular oxygen and hydrogen peroxide as oxygen precursors: Structural and optical properties. *Solar energy materials and solar cells, 91(15-16), 1458-1461.*

[14]. Salim, H. I. and Olusola, O. I.and Madugu, M. L. (2017). Effect of thickness: a case study of electrodeposited CdS in CdS/CdTe based photovoltaic devices *Journal ofMaterial Science Material Electron., 28, (4) 3254–3263, 2017,*

[15]. Xu, H. Y., Liu, Y. C., Xu, C. S., Liu, Y. X., Shao, C. L., and Mu, R. (2006). Structural, optical, and magnetic properties of Mn-doped ZnO thin film. *The Journal of chemical physics, 124(7). s*

Table 1 Percentage Atomic Composition of Electrodeposited ZnO-MgO Nano-Composite Thin Films Grown at Various Bath pH Values.

Bath pH	**Zn (g)**	**Mg (g)**	**O (g)**	**Zn/Mg (g)**	**Zn/O (g)**	**Mg/O (g)**
4.0	4.5	7.0	41	0.64	0.10	0.17
5.0	5.6	12.6	50	0.44	0.11	0.25
6.0	13.3	29.9	49.2	0.44	0.27	0.60

Table 2 Average Structural Properties of Electrodeposited ZnO/MgO (ZG) Nano-Composite Thin Films

Thin Films pH	**Crystallite size (nm)**	**Micro-strain, ε $x10^{-3}$**	**Dislocation density, δ $x10^{15}(nm)^{-2}$**	**Thickness of film (nm)**
4.0	12.561	8.833	3.366	341
5.0	12.510	9.059	10.101	386
6.0	12.034	9.297	10.150	451

Table 3 Average Results of Refractive Index, Optical Conductivity, and Band Gap of ZnO /MgO (ZG) Nano-Composite Thin Films

Thin films pH	**Refractive index (n)**	**Optical conductivity (σ) ($1X10^{11}$) s^{-1}**	**Band gap (E_g) (eV)**
4.0	1.859	7.250	3.28
5.0	1.966	9.534	3.26
6.0	2.226	11.449	3.12

Table 4 Average Results of Absorbance, Reflectance, and Transmittance of ZnO -MgO (ZG) Nano-Composite Thin Films

thin films pH	**Absorbance (A) (arb. Unit)**	**Reflectance (R) (arb. Unit)**	**Transmittance (T) (arb. Unit)**	**A + R + T**
4.0	0.150	0.034	0.816	1
5.0	0.200	0.071	0.729	1
6.0	0.343	0.095	0.562	1

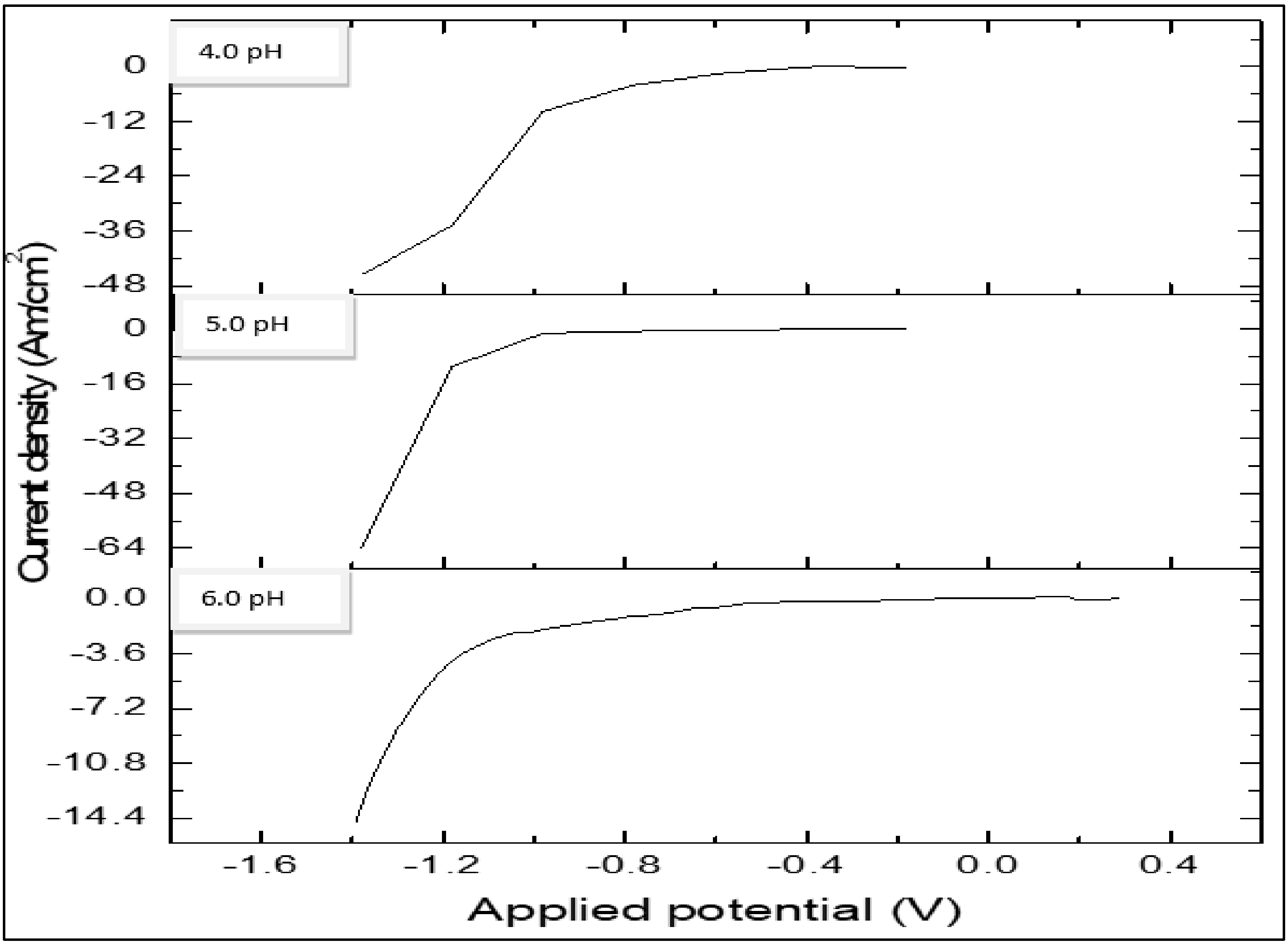

Fig 1 Cyclic Voltammograms on FTO Coated Glass Substrate in a Bath Mixture of 40% 40mM Zinc Nitrate and 60% 40mM Magnesium Nitrate Solution

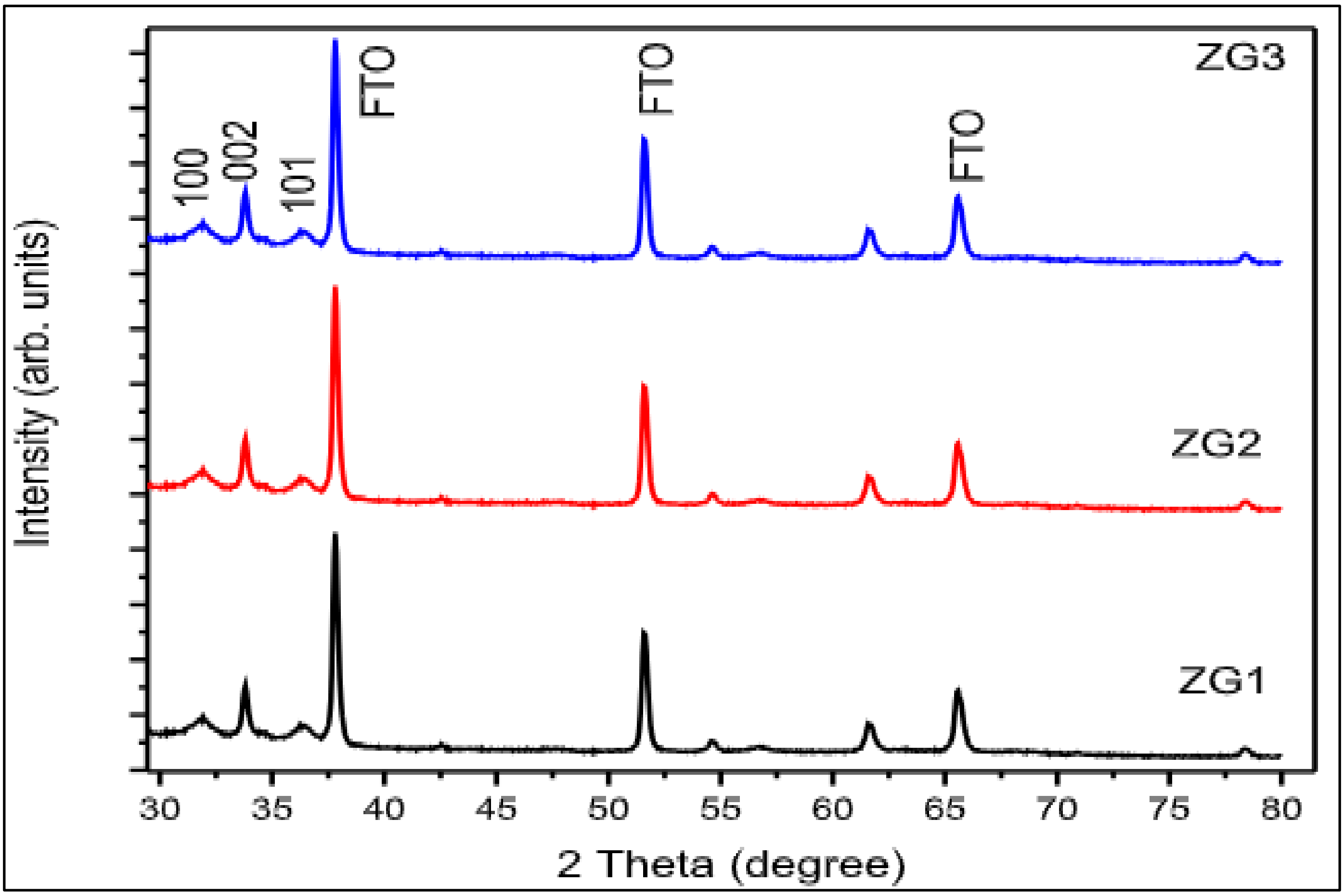

Fig 2 X-Ray Diffraction Patterns of Electrodeposited ZnO/MgO Nano-Composite Films Electrodeposited

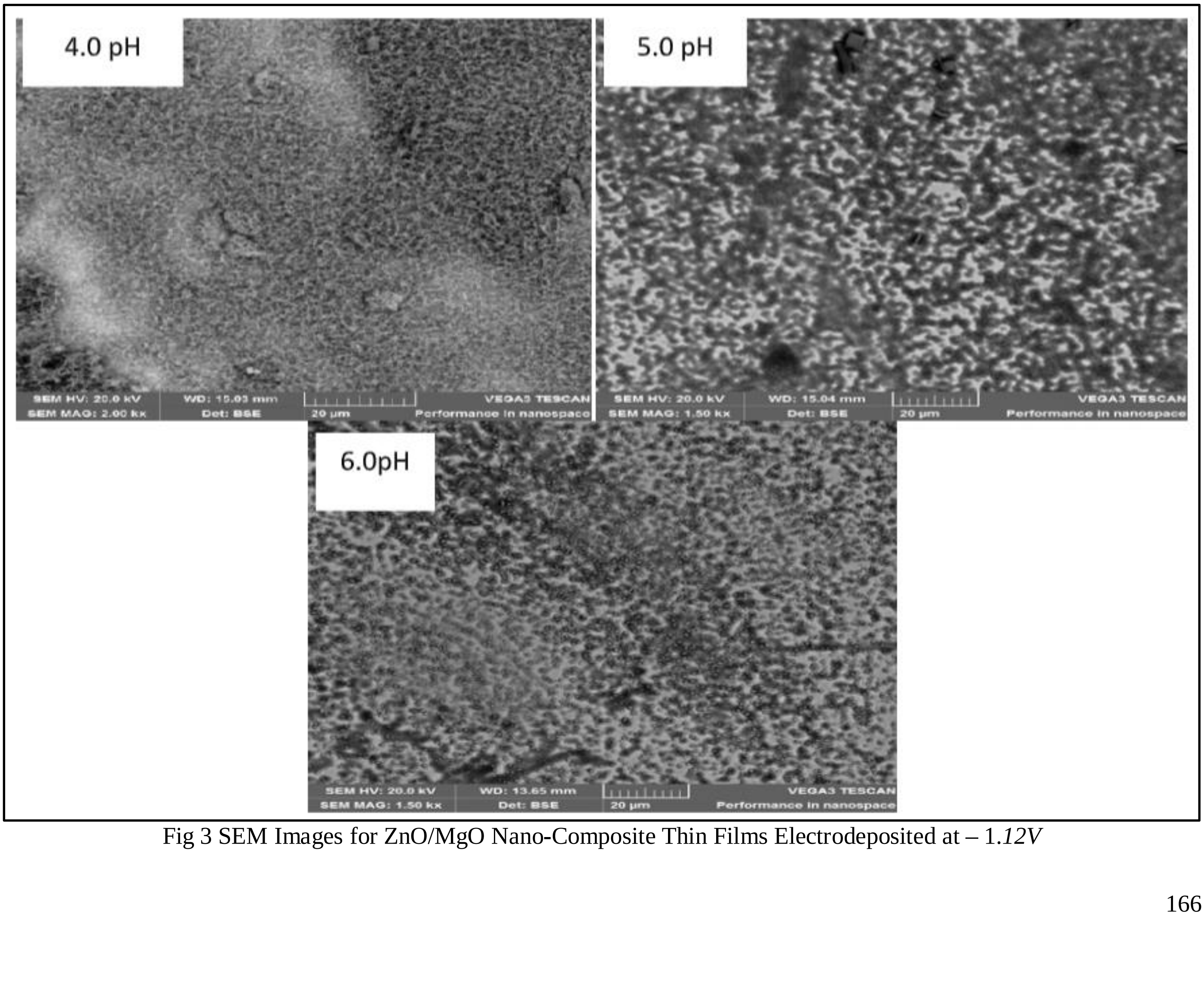

Fig 3 SEM Images for ZnO/MgO Nano-Composite Thin Films Electrodeposited at – 1.*12V*

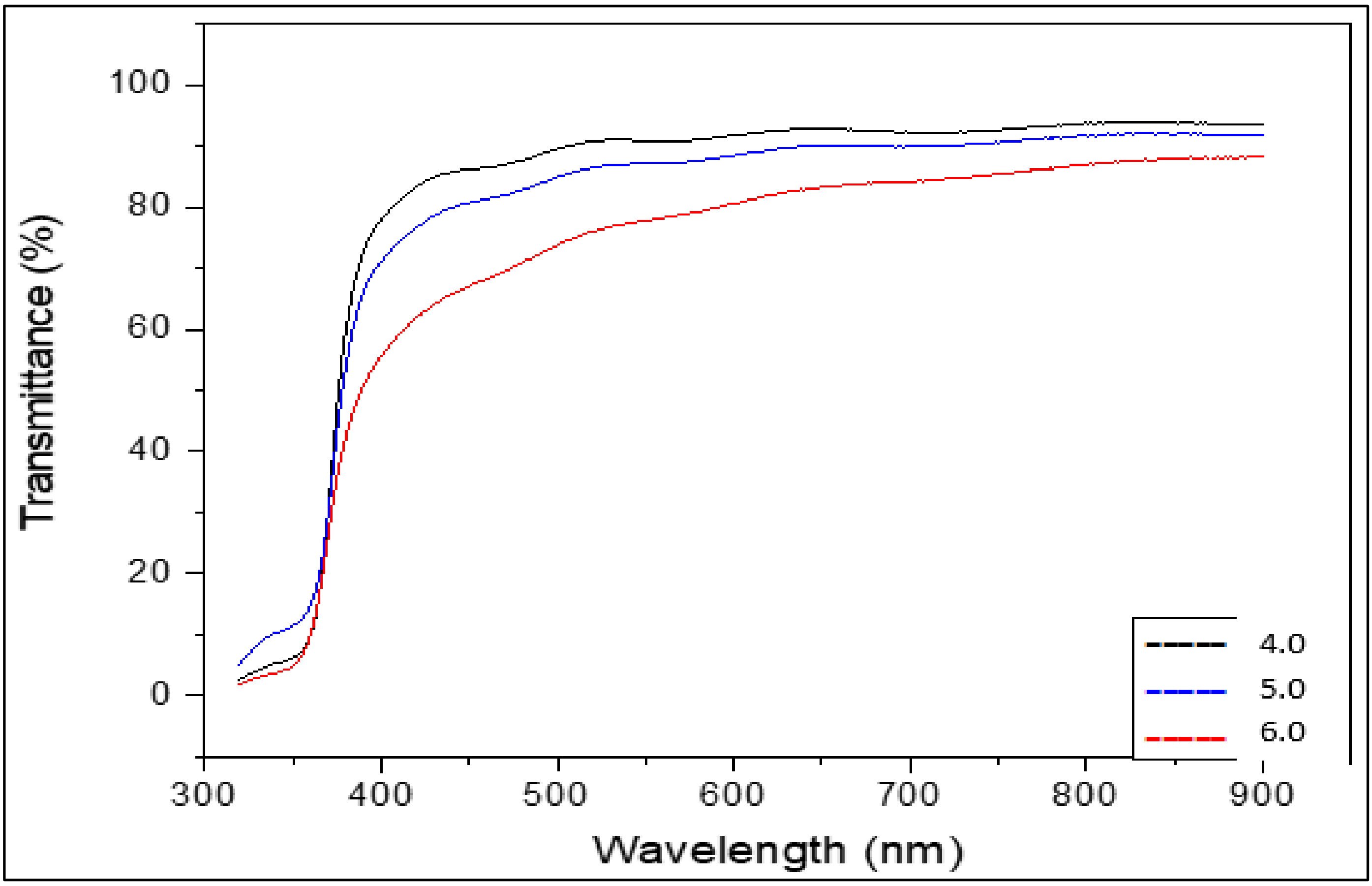

Fig 4 Transmission Spectra for ZnO/MgO Nano-Composite thin Films at Various Bath pH Values of 4.0,5.0 and 6.0.

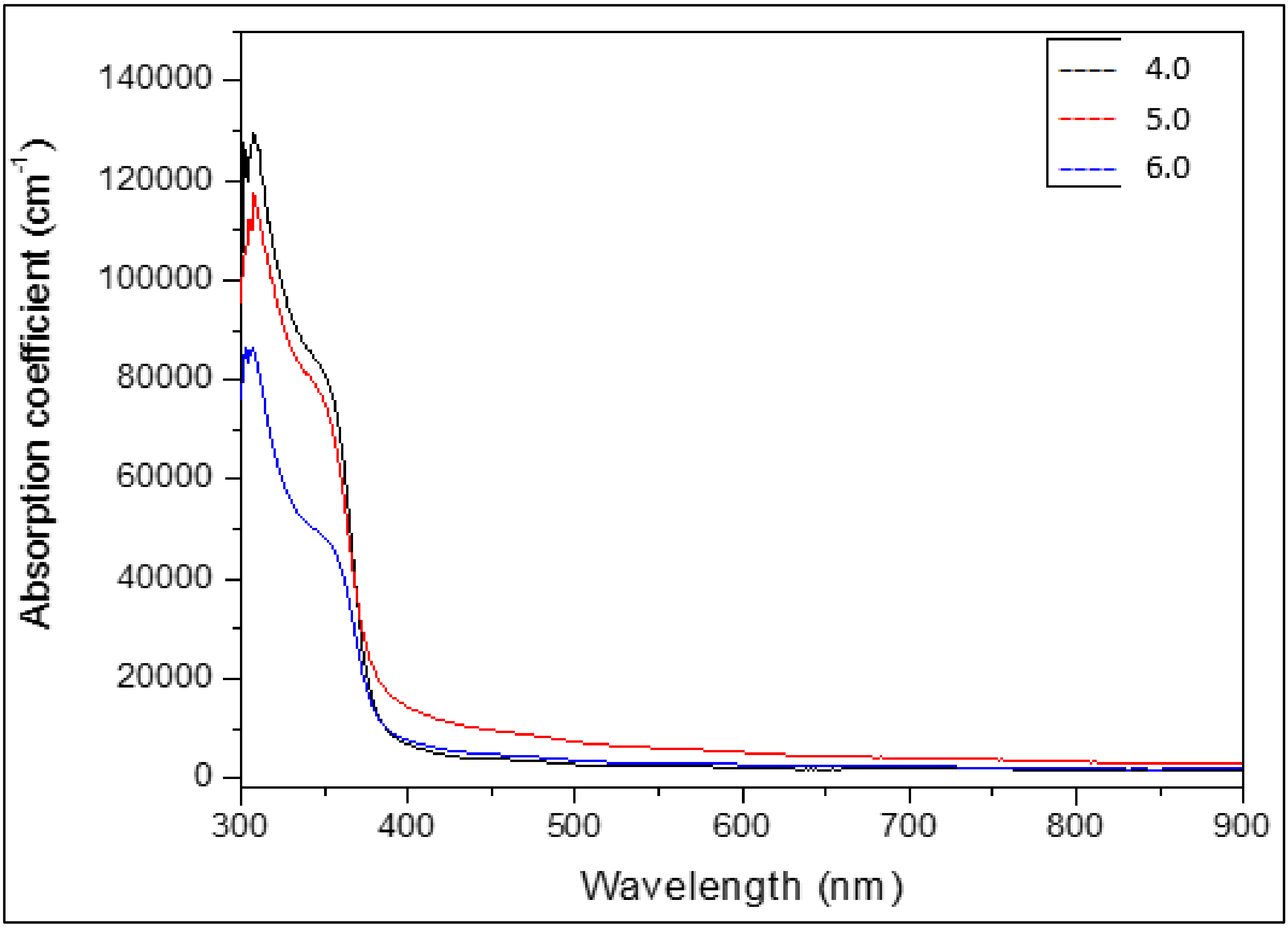

Fig 5 Absorption Coefficient for ZnO/MgO Nano-Composite Thin Films at Different Bath pH Values of 4.0, 5.0 and 6.0.

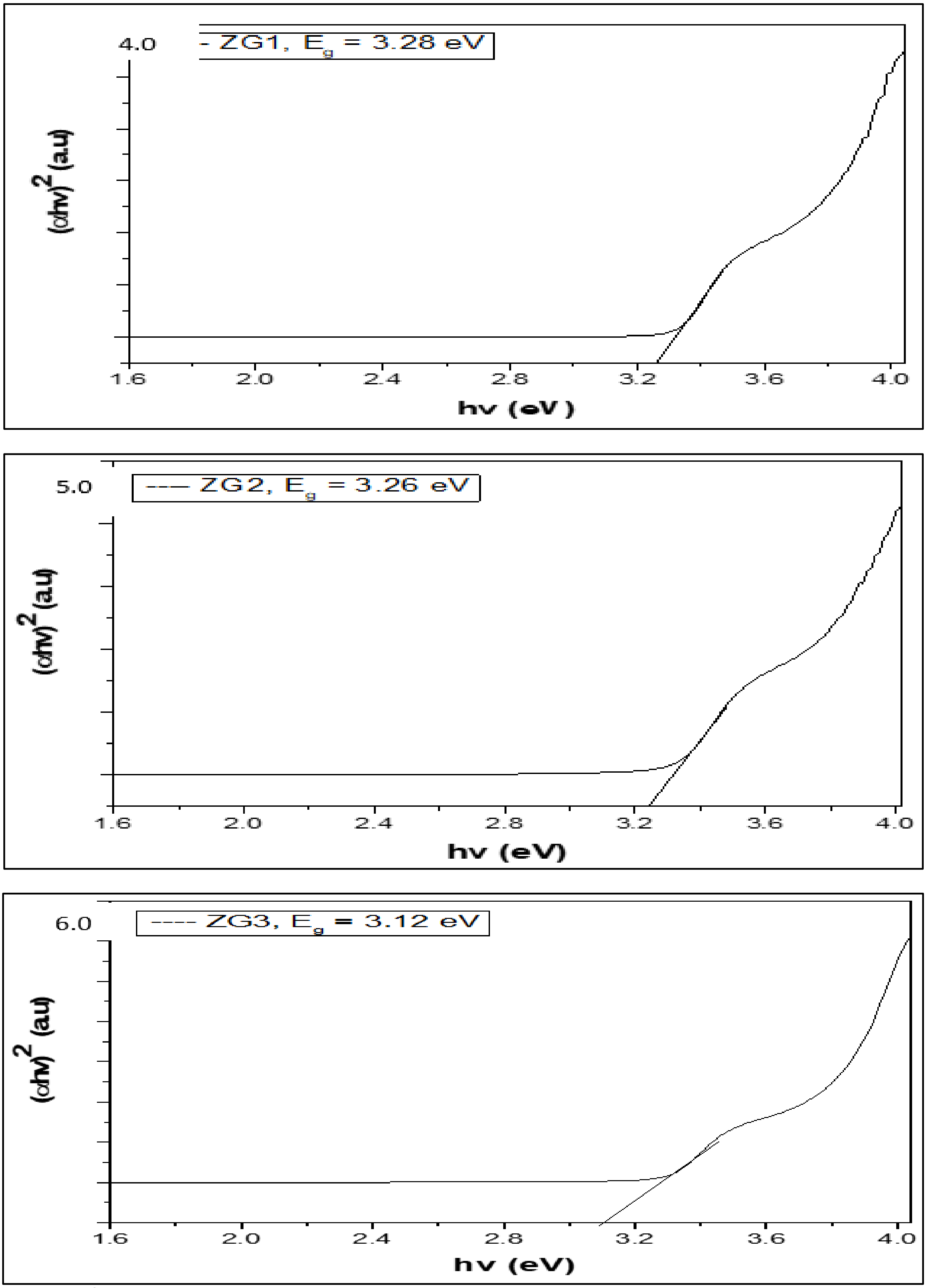

Fig 6 $(\alpha h\nu)^2$ Versus Photon Energy (hν) for ZnO/MgO Nano-Composite Thin Films Deposited at Different Bath pH of 4.0, 5.0 and 6.0

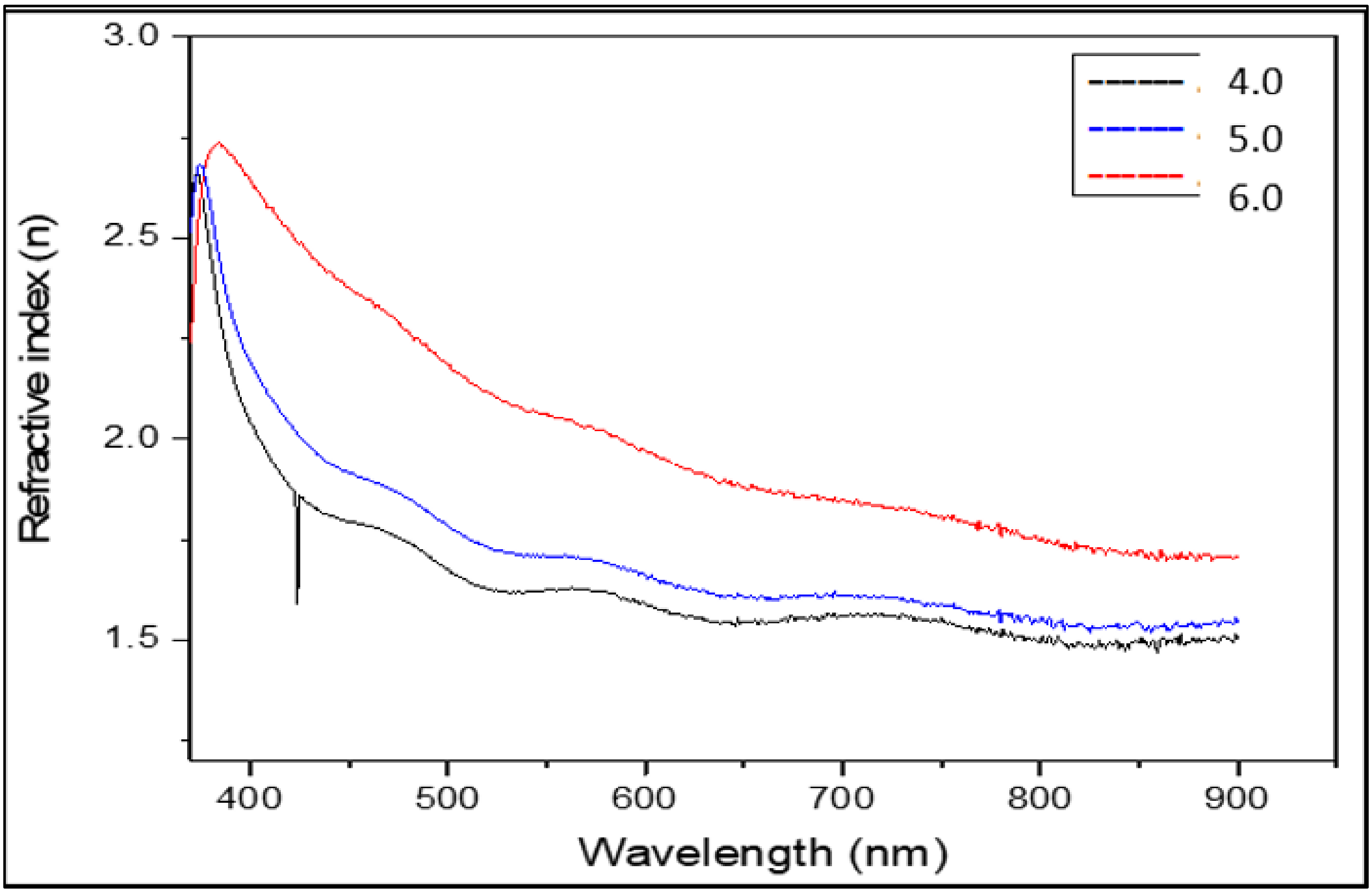

Fig 7 Refractive Index Versus Wavelength for Electrodeposited ZnO/MgO Nano-Composite Thin Films

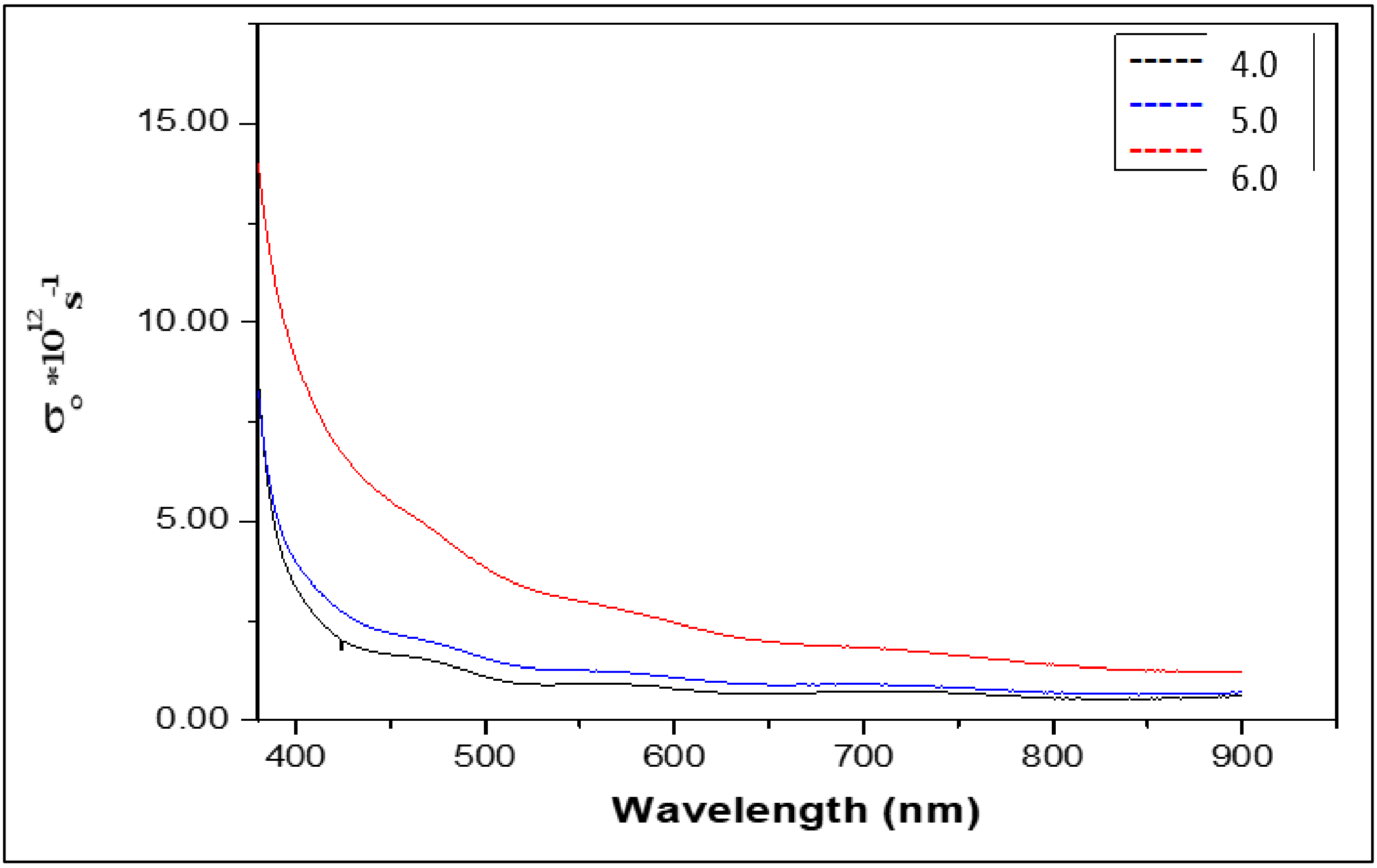

Fig 8 Optical Conductivity (σ) Versus Wavelength for Electrodeposited ZnO/MgO Nano-Composite Thin Film at Different Bath pH of 4.0, 5.0 and 6.0.