The effect of Zn$^{2+}$ on the anion vacancies in ZnO thin-films grown using chemical bath deposition.

F V Molefe$^{1,2,*}$, S J Mofokeng$^1$, M Khenfouch$^{1,2}$, M Achehboune, M S Dhlamini$^{1,2}$, B M Mothudi$^{1,2}$ and L F Koao$^3$.

$^1$Department of Physics, University of South Africa, Private Bag X90, Florida, 1710, South Africa.

$^2$Africa Graphene Centre, Department of Physics, University of South Africa, Private Bag X90, Florida, 1710, South Africa.

$^3$Department of Physics, University of the Free State (Qwaqwa campus), Private Bag X13 Phuthaditjhaba, 9866, South Africa.

$^*$E-mail: volksfmv@gmail.com

Abstract. Zinc Oxide (ZnO) thin-films were grown on glass substrate using chemical bath deposition method (CBD) from precursors containing varying molar concentrations of zinc acetate. The structure, morphology, optical and luminescence properties of the films were investigated using X-ray diffraction (XRD), Scanning electron microscopy (SEM), Ultraviolet visible spectroscopy (UV/VIS/NIR) and Photoluminescence spectroscopy (PL). The XRD result showed that at low molar concentrations of zinc acetate the structure consists of Zn(OH)$_2$ and ZnO phases. As the molar concentration of zinc acetate increases the well-known hexagonal wurtzite structure of ZnO was developed. The average crystallite size estimated using Scherrer’s formula was about 41.19 nm. It was found that the average crystallite size increased with an increase in the molar concentration of zinc acetate. SEM observations showed the presence of nanoparticles forming aggregated nanoflakes. The surface morphology was found to be dependent on the concentration of zinc acetate. The UV-Vis spectra showed that the absorption band edge shift to the higher wavelength with an increase in molar concentration of zinc acetate. The band gap energy of ZnO thin-films determined from UV reflectance spectra was found to decrease from 3.17 to 2.73 eV with an increase in the zinc acetate concentration. The PL results showed that the luminescence intensities decrease with an increase in the molar concentration of zinc acetate without any noticeable shift in position.

Keywords: zinc acetate; thin-films; chemical bath deposition (CBD), ZnO.

1. Introduction

Semiconductors with dimensions in the nanometer realm are important because their electrical, optical and chemical properties can be tuned by changing the size of the particles. The properties of these semiconducting nanomaterials include large specific surface area and high reaction activity [1]. Optical properties are of great interest for application in optoelectronics, photovoltaics and biological sensing [2–3]. Zinc oxide has attracted significant interest because of its nontoxic character, chemical stability, low cost and potential applications in many technological fields [4–5]. ZnO is known to be n-type semiconductor with a wide band gap of 3.37 eV at room temperature and a large exciton binding energy of about 60 meV [6]. Various chemical synthetic methods have been developed to prepare such nanostructures including sol-gel spin coating method [7], pulsed laser deposition method (PLD) [8], and sonochemical method [9]. In our study CBD method was used to grow ZnO thin-films...
at different concentrations of zinc acetate. CBD is one of the solution phase methods useful for the preparation of compound semiconductors from aqueous solutions [10]. The CBD method has several advantages such as the use of simple equipment, cost effective, less hazardous and the low temperature reaction. The low reaction temperature makes this method attractive and the particle properties such as morphology and size can be controlled via the CBD process by adjusting the synthesizing time and temperature [11]. Most of the conducted research on ZnO prepared by CBD mainly focused on morphology and electrical properties [12], but our research focuses on luminescent properties. Cao et al [13] prepared single-crystal ZnO nanosheets (independent of substrates) in bulk quantity from a soft aqueous solution by controlling the nucleation and crystal growth process in CBD methods. They observed a sharp UV excitonic PL band centered at 380 nm with a negligible green emission. Therefore, it is worthwhile to investigate the relationship between the structure and luminescent properties of ZnO thin-films prepared by CBD method.

In the work described here, the influence of zinc acetate concentration on the structure, optical and luminescent properties of ZnO thin-films is investigated at low reaction temperature of CBD (80 °C) for period of 10 min. The results provided some important indications, such that zinc acetate concentration has great influence on structure optical and luminescent properties for extending optical and luminescent applications.

2. Experimental
The ZnO thin-films were grown using chemical bath deposition method. The following starting materials: zinc acetate (Zn(O₂CCH₃)₂), Thiourea ((NH₂)₂CS) and Ammonia (25% NH₃) were used. The sample solutions were prepared by dissolving 0.12, 0.13 and 0.14 M of zinc acetate in 60 ml of deionized (DI) water each, respectively, and 0.4 M of thiourea and also 98.8ml of ammonia, were dissolved into 200 ml of DI water, respectively. Then a magnetic stirrer was used to stir each of the mixtures overnight at room temperature to ensure homogenous distribution of the solution reagents. An equal volume ratio (1:1:1) was considered for each solution in the following order: 60 ml quantity of zinc acetate was first added to the beaker which was placed in the water bath, followed by addition of 60 ml of thiourea solution while stirring and finally 60 ml of ammonia solution was also added while continuously stirring. Water bath was maintained to be at a constant desired temperature of 80 °C. The white precipitates were then formed within 30 seconds after the solution was placed inside the water bath. Then for the growth of ZnO thin-films, the masked glass substrates were immersed vertically after mixing the precursors in the glass beaker. The glass substrates were removed from beaker inside the bath after 10 minutes of deposition. Finally, the obtained thin-films were dried at 130 °C for 10 min on magnetic hot plate prior characterization. The grown thin-films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS), ultraviolet visible near-infrared (UV/VIS/NIR) spectroscopy and Photoluminescence (PL) spectroscopy.

3. Results and Discussion
3.1 Structural analysis
Figure 1 shows XRD patterns of ZnO thin-films grown at various molar concentrations of zinc acetate. As indicated in these patterns, the prepared ZnO thin-films exhibit the mixture of two phases. At low molar concentration of zinc acetate (0.12 M) there are two diffraction peaks at 20 values 33.5° and 59.5° marked with asteriks (*) corresponding to Zn(OH)₂ in agreement with data from JCPDS card (No. 38-0356). The major diffraction peaks at 20 values of 31.8°, 34.5°, 36.4°, 47.5°, 56.2°, 62.9° and 69.1° consistent with the standard JCPDS card (No. 36-1451) for hexagonal wurtzite ZnO are observed. Upon increasing zinc acetate concentration to 0.13 M, Zn(OH)₂ peaks diminishes, the possible reason for these observation can be due to dehydration of OH⁻ from Zn(OH)₂ when more Zn²⁺ are introduced into the material. These happen through the formation mechanism because zinc species present in the solution were not sufficient for the nucleation and growth of ZnO [14]. The solid-solid phase transformation from Zn(OH)₂ to ZnO takes place. Thus, Zn²⁺ atoms enter the crystal structure of Zn(OH)₂ which is more open (packing density of 44.4 % compared to 53.3 %
of ZnO) [15]. Then the dehydration process takes place amongst every two nearest hydroxyl groups. When dehydration takes place, each oxygen ion sees a tetrahedral coordination with four zinc ions. Finally, the contraction and rearrangement of atoms in the lattice structure takes place and result in the formation of a hexagonal wurtzite structure of ZnO [16]. Furthermore, at high zinc acetate concentration 0.14 M ZnO diffraction peaks are more intense and sharp compared to lower concentrations, and this indicates the clear formation and crystallization of ZnO structure. Thus, the increase in molar concentration of zinc acetate plays an important role on the growth of ZnO thin-films because Zn(OH)$_2$ has decomposed into hexagonal wurtzite structure. The calculated average lattice parameters are $a = 3.249$ and $c = 5.206$ Å which match well with those of hexagonal wurtzite structure of ZnO. The average grain size of the ZnO thin-films was estimated using the full width at half maxima (FWHM) from the line broadening of the (100), (002), (101), (102), (110) and (103) XRD peaks. The Debye Scherrer’s formula was used to estimate the mean grain size of the thin-films grown at 0.13 and 0.14 M zinc acetate concentrations which were found to be 38.81 and 43.56 nm. These results indicate that the size of the particles increased as zinc acetate concentration increases. The increase in size of ZnO particles has also been noticed by Koao et al [17] as the concentration of zinc acetate increases. It is believed that the increase in particle size is due to the “Ostwald ripening process” [17], which is the observed phenomenon in solid and liquid solutions used to describe the evolution of inhomogeneous structures. Joshi et al [18] obtained nano-crystalline ZnO and the average crystal size decreased with increasing zinc acetate dehydrates concentration.

![XRD patterns for ZnO thin-films grown at different molar concentration of zinc acetate using CBD method.](image)

**Figure 1.** XRD patterns for ZnO thin-films grown at different molar concentration of zinc acetate using CBD method.

### 3.2 Surface morphological analysis

Figure 2 (a) and (b) shows surface morphology of the ZnO thin-films grown at various molar concentrations of zinc acetate. The surface aspects of all the SEM images of the ZnO thin-films are composed of nano flakes structures and the grain size appears to increase slightly in size with an increase in the molar concentrations of zinc acetate. At low molar concentration of zinc acetate (0.12 M) the nano flakes are non-uniform while at high molar concentration (0.14 M) the nano flakes have uniform morphology shown in Figure 2(a) and (b), respectively. Zhang et al [19] obtained worse-aligned, rough, and disordered irregular nanorods shapes which changed into perpendicular smooth nanoflakes as zinc acetate concentration increases using hydrothermal method. Baviskar et al [20] observed highly nano-porous structures which became clustered as the solution concentration increases when studying the effect of zinc acetate concentration on the morphology of ZnO.
3.3 Compositional analysis

The elemental composition analysis of ZnO thin-films grown at various molar concentrations of zinc acetate carried out using an EDS integrated with SEM instrument are shown in Figure 3. EDS spectrum demonstrated that thin-film grown at 0.12 M contains Oxygen (O), Sulphur (S) and Zinc (Zn) in addition to Carbon (C) from the carbon tape. The observed S comes from one of the precursors ((NH₂)₂CS). For the sample prepared at 0.13 and for 0.14 M only C, O and Zn were observed and no other impurity were present. This shows that the amount of S vanished with the increase in concentration of zinc acetate. At the top right corner of each spectra there is a bar graph used to compare the weight % of elements in the sample. The concentrations of Zn, S and O for sample prepared at 0.12 M are ~ 65, 32 and 3 %, respectively. The concentrations of Zn and O were 67 and 33 % for 0.13 M and 75 and 25 % for 0.14 M. Thus, the amount of Zn increased while O decreased with the increase in content of zinc acetate. This relates back to XRD results, wherein the amount of O decreased during dehydration of OH⁻ while the Zn was increased when adding more zinc acetate concentration.
3.4 Optical properties

Figure 4 (a) shows the diffuse reflectance spectra of ZnO thin-films grown at various molar concentrations of zinc acetate. The spectra reveals high uniform percentage reflectance at ~ 92 % in the visible region and high absorption in the ultraviolet (UV) region. In the UV region for ZnO thin-film grown at 0.12 M there are three (3) small nonhomogeneous absorption edges. The observed absorption is increased with an increase in the molar concentration. Preda et al [21] noticed a strong decrease of percentage reflectance in all the spectra which is linked to the band-to-band transition in ZnO. Furthermore, there is a redshift in band-to-band transition as the molar concentration of zinc acetate increase. The ZnO is a direct band gap material. The energy band gap of these materials was estimated using the Kubelka-Munk remission function [17].

In Figure 4(b) the energy band gaps were measured with the help of reflectance spectra plotting graphs of \((K\nu)\alpha\) versus \(f(\nu)\) [22]. Fitting of the linear portion of the plot to photon energy \((h\nu)\) axis gives the band gap of ZnO. The direct band gap energy values obtained for ZnO were 3.17, 2.90 and 2.73 eV, respectively. It is evident that the band gap energy of the ZnO thin-films decreases with an increase in the molar concentration of zinc acetate. This shift of absorption edge to higher wavelength and the reduction of band-gap energy may be attributed to the decomposition of Zn(OH)\(_2\) to the hexagonal wurtzite ZnO as seen in the XRD analysis. Secondly it may be due to the grain size increase observed in XRD results as the molar concentration of zinc acetate increases.
3.5 Photoluminescence

Figure 5 depicts the room temperature emission spectrum of the ZnO thin-films acquired at an excitation wavelength of 300 nm. The maximum emission intensity was obtained at the ZnO thin-film grown at 0.12 M of zinc acetate. The broad symmetric emission band between 400 and 600 nm was observed which can be attributed to transition between singly charged oxygen vacancy \((V_0)\) and photo excited hole or zinc interstitial (\(Zn_i\)) related defects [2324]. This is in agreement with EDS results, wherein the amount of Zn increased while increasing zinc acetate concentration. From the spectra, the intensity of PL peak decreases as molar concentration of zinc acetate increases. For all the thin-films the blue emission peak at 464 nm is observed. There was no shift in luminescence band as the molar concentration of zinc acetate increases. The higher molar concentration of zinc acetate results in a substantial decrease in luminescence intensity. This decrease in luminescence intensity firstly: may be due to the grain sizes that are increasing with increasing the molar concentration of zinc acetate as confirmed by SEM analysis and secondly may be attributed to decomposition of Zn(OH)\(_2\) to the hexagonal wurtzite ZnO as confirmed by the XRD analysis. The study by Molefe et al [25] indicates a decrease in blue luminescence intensity of ZnO prepared by CBD method when changing the reaction time. Florica et al [26] indicated that quenching of ZnO emission is due to dehydration of Zn(OH)\(_2\) during formation of ZnO when using chemical methods such as CBD.

Figure 5. PL emission spectra of ZnO thin-films grown at various molar concentrations of zinc acetate using CBD method.
Conclusion

It was feasible to grow thin-films of ZnO using CBD method at various molar concentrations of zinc acetate. Increasing zinc acetate concentration showed great effect on structural, morphological, optical and luminescent properties of ZnO thin-films. XRD showed that as the molar concentration of zinc acetate increases Zn(OH)₂ decompose into hexagonal wurtzite ZnO. SEM images depict homogenous ZnO nanoflakes at high molar concentration of zinc acetate. The band gap energy of the ZnO thin-films decreases with an increase in the molar concentration of zinc acetate. The PL intensity was found to be maxima for thin-films grown at 0.12 M and decreased at 0.13 and 0.14 M concentrations of zinc acetate.

Acknowledgements

This work was supported financially by the National research Foundation (NRF) of South Africa in the College of Science Engineering and Technology (CSET) at the University of South Africa (UNISA).

References

[1] El-Morshedi N, AlZahrani I, Kizilbash N.A. and Al-Fayez H A A 2014 Int. J. Adv. Res. 2 907 – 915
[2] Weißenrieder K S, Muller-J, 1997 Thin Solid Films, 300 30
[3] Masai H, Toda T, Ueno T, Takahashi Y, Fujiwara T, 2009 Appl. Phys. Lett. 94 151908
[4] Fan Z, Wang D, Chang P, Tseng W, Lu JE. 2004 Appl. Phys. Lett. 85 5932
[5] Trupke T, Green M A, Wurfel P, 2002 J. Appl. Phys. 92 1668
[6] Djurišić AB, Ng AMC, Chen XY, Prog. 2010 Quant. Electr. 34 191
[7] Foo K.L, Kashif M, Hashim U and Ali M E 2013 Current Nanoscience. 9 1 – 5
[8] Dai Z-H, Zhang R-J, Shao J, Chen Y-M, Zheng Y-X, Wu J-D and Chen L-Y 2009 J. Korean Phys. Soc.55 1227 – 1232
[9] Kumar Vinod, Swart H.C, Gohain M, Kumar Vijay, Som S, Bezuindenhoudt B C B and Ntwaeborowa O M 2014 Ultrason. Sonochem. 21 1549 – 1556
[10] Duran P, Capel F, Tartaj J, Moure C 2002 Adv. Mater. 14 137 – 141
[11] Behera J K, MSc thesis, National Institute of technology, India. pp. 11 – 35
[12] Chu D, Hamada T, Kato K and Masuda Y 2009 Phys. Status Solidi A 206 718 – 723
[13] Cao B, Cai W, Li Y, Sun F and Zhang L 2005 Institute Of Physics Publishing Nanotechnology 16 1734 – 1738
[14] Jia W, Dang S, Liu H, Zhang Z, Yu C, Liu X and Xu B 2012 Mat. Lett. 99 – 101
[15] Wang M, Zhou Y, Zhang Y, Hahn H S and Kim E J 2011 Cryst. Eng. Comm. 6024
[16] Cornell R.M and Schwertmann U 1996 VCH, Weinheim
[17] Koao L.F, Dejene F.B and Swart H.C 2014 Mater. Sci. Semicond. Process. 27 33 – 40
[18] Joshi B.N, Yoon H, Kim H.Y, Oh J.H, Seong T.Y, James S.C and Yoon S.S 2012 J. Electrochem. Soc. 159 H716 – H721
[19] Zhang J, Gao D, Yang G, Zhu Z, Zhang J and Shi Z 2012 Int. J. Mech. Mat. Eng. 38
[20] Baviskar P, Ennaoui A and Sankapal B 2014 Solar energy 105 445 – 454
[21] Preda N, Enculescu M, Florica C, Costas A, Evangelidis A, Matei E and Enculescu I 2013 Dig. J. Nanomater. Bios. 8 1591 – 1600
[22] Tauc J, Grigorovici R, Vancu Sharma A, 1966 Phys. Status Solidi. 15 627 – 629
[23] Vanheusden K, Warren W L, Seager C H, Tallant D R, Voigt J A, Gnade B E, 1996 J. Appl. Phys. 79 7983 – 7990
[24] Peng W Q, Qu S C, Cong G W, Wang Z G, 2006 Mater. Sci. Semicond. Process. 9 156
[25] Molefe F.V, Koao L F, Dolo J J and Dejene B F 2014 Physica B 439 185 – 188
[26] Florica C, Preda N, Enculescu M, Zgura I, Socol M and Enculescu I 2014 Nanoscale Res. Lett. 9 385 1 – 10