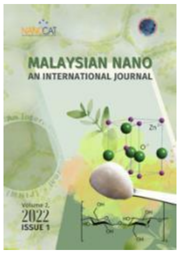
Malay. NANO Int. J. Vol 2(1) (2022) 46 - 54

Malaysian NANO-An International Journal



Research Article

Surface Wettability of ZnO Thin Films

M.R.Y. Hamid [a], A. Ma'amor [b], B.H. Ong [a,*]

Affiliations:

[a]Nanotechnology & Catalysis Research Centre (NANOCAT), Institute for Advanced Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia.

[b]Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

Received June 5, 2022
Revised July 27, 2022
Accepted July 30, 2022

DOI:
https://doi.org/10.22452/mnij.vol2no1.3

Corresponding authors:
bhong@um.edu.my

Abstract

In this study, zinc oxide (ZnO) structured films were grown on glass substrates using a simple chemical bath deposition (CBD) method with different salt precursors. The variation of salt precursors towards the surface morphology of thin films and its wettability properties were investigated. Four types of zinc (Zn) salt used as precursors are zinc chloride ($ZnCl_2$), zinc acetate ($ZnAc_2$), zinc nitrate ($Zn(NO_3)_2$) and zinc sulfate ($ZnSO_4$). The crystallinity of ZnO thin films was evaluated using X-ray diffraction (XRD), and the surface morphology was observed using field emission scanning electron microscopy (FESEM). Finally, the wettability was determined by contact angle (CA) measurement. It was found that $ZnCl_2$ has the lowest CA (127.1°), while $ZnSO_4$ exhibits the highest CA (142.3°). The Zn salts used significantly influenced the thin film surface morphology, resulting in varied wetting behaviour depending on the surface roughness.

Keywords*:* salt precursor; low temperature; thin film; hydrophobic; surface roughness

1. Introduction

Zinc oxide (ZnO) is a II-VI semiconductor with a wurtzite hexagonal structure. It has a wide direct bandgap (3.37 eV) and exhibits large exciton binding energy (60 meV) at room temperature [1-4]. ZnO held several unique properties, such as being environmentally benign, abundant, inexpensive, intense ultraviolet absorption capacity, and potent antimicrobial activity [5]. These properties cause ZnO heavily explored in various fields such as photodetectors, anti-reflective coatings, light-emitting diodes (LEDs), gas sensing devices, field-effect transistors (FETs) and solar cells [6-8]. The standard methods used to prepare ZnO thin films are sol-gel, spray pyrolysis, chemical vapour deposition, wet chemical deposition, hydrothermal method, electrochemical, and pulsed laser deposition [7, 9-10]. However, chemical bath deposition (CBD) is more appealing as it can be conducted at low temperatures and offers a fast and simple route preparation. Moreover, it can be scaled up to meet industrial needs [7, 10].

To widen the functionality of ZnO structures by controlling their properties is always preferred. Surface wettability is one of the essential properties that covers every aspect of many industrial processes, from agriculture, medicine, food packaging, painting, and printing to oil recovery [11]. Tuning surface wettability can be achieved by modifying surface energy or morphology [12]. For instance, in optoelectronic applications, the self-cleaning properties of semiconductor metal oxide thin films with different morphologies have been a subject of focus [10]. Surface wettability can be elucidated as the interlinkage between a liquid and a solid surface. It can be determined by measuring the contact angle (CA) based on the spreading behaviour of liquid drop onto a solid surface. The CA value relies upon the surface tension and the roughness of the solid substrate [13]. The correlation between surface topography and microstructure, surface free energy, and chemical composition will define the wetting behaviour of a thin film. Surfaces with water contact angles < 90° are hydrophilic, while those with contact angles ≥ 90° are hydrophobic [10].

In this work, the ZnO thin films will be deposited on glass substrates via the CBD technique by following the procedure from the previous work [14]. To obtain different morphologies of ZnO thin films, different types of zinc (Zn) salts, i.e. zinc chloride ($ZnCl_2$), zinc acetate ($ZnAc_2$), zinc nitrate ($Zn(NO_3)_2$) and zinc sulfate ($ZnSO_4$) are used as precursors. Permanganate treatment is applied beforehand to improve adhesion of the films, while the concentration, deposition time and temperature parameters will be fixed throughout the experiment. In addition, the influences of the different Zn salt on the morphological, structural, and hydrophobic properties of the ZnO thin films are also reported.

2. Materials and Methods

Materials

Soda-lime microscope slide glass was used as substrates to grow ZnO thin films via the CBD method in a water bath (Memmert). The glass substrates were scribed using a diamond scriber in a 1.5 cm x 2 cm dimension. The glass substrate needs to be put upslope to the sidewall of the vial to steer clear of the accumulation of bulk precipitation. Analytical grade of potassium permanganate ($KMnO_4$, Sigma-Aldrich), 99.8% *n*-butanol (C_4H_9OH, Merck), zinc chloride hexahydrate ($ZnCl_2.6H_2O$, Friendemann Schmidt), zinc acetate dihydrate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$, Merck), zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, Friendemann Schmidt), zinc sulfate heptahydrate ($ZnSO_4.7H_2O$, Sigma-Aldrich), ethanolamine (C_2H_7NO, Sigma-Aldrich) and ammonium hydroxide (NH_4OH, Merck) was used as received without any further purification. The sonication processes were done using an ultrasonic bath (Thermo-Line) with distilled water (DW) as a cleaning solution.

Synthesis

The details of the synthesis procedure have been previously described elsewhere [14]. In brief, the deposition solution was prepared by diluting the previously prepared stock solution; 1.0 M zinc chloride, 1.0 M zinc acetate, 1.0 M zinc nitrate, 1.0 M zinc sulfate, 4.0 M ammonia solution and 50% v/v ethanolamine. The final deposition solution contains 0.1 M Zn salts, 0.4–0.6 M ammonia solution and 10% v/v ethanolamine. The glass substrates were cleaned using ethanol and DI water before being sonicated for several minutes.

First, the surface of the substrates needs to be activated with 50 mM $KMnO_4$ solution added with 2 mL of *n*-butanol as a reducing agent before being placed in a water bath for 20 min at 85 °C. The permanganate-treated thin film was rinsed thoroughly several times using the DW water. Then, the diluted ZnO deposition solutions are poured into the glass vial to immerse the activated glass substrate before being placed in the water bath at 85 °C for 40 min. Lastly, the glass substrates are dried in an oven after being carefully collected. The following procedure was repeated using other Zn salts. The process flow to fabricate ZnO thin film was schematically shown in Figure 1.

Characterization

The X-ray diffraction (XRD) measurements were carried out using a PANalytical Empyrean with a Cu Kα radiation (k = 1.5406 Å) at 40 kV and 40 mA for the operating voltage and current, respectively. The scanning was performed with a step size of 0.013 in a 2θ range of 20° to 80°. The surface morphology was observed by a field emission scanning electron microscope (FESEM) using

Hitachi SU8030 following the sputtering of the samples with a thin layer of Platinum (Joel JEC-3000FC) to eliminate excessive charges. The wettability of the ZnO thin films was quantified by measuring the drop shape analyzer, DataPhysics model OCA 15EC. A water droplet with a volume of 3 μL is set to dispense on the thin film. The CA value of each sample represents the average of three measurements at different locations on the surface.

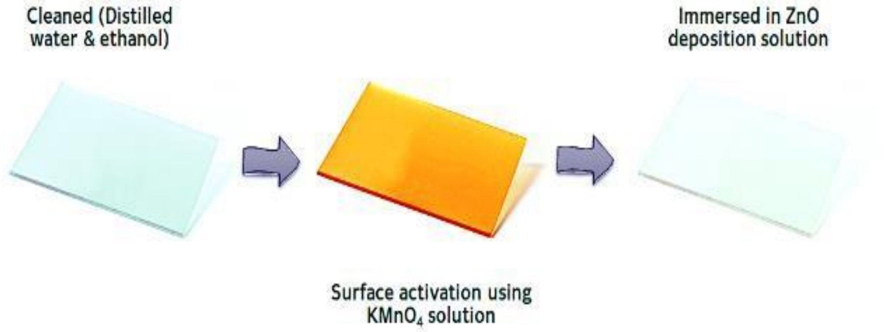


Figure 1: Schematic diagram of ZnO thin film fabrication using CBD method.

3. Results and discussion

Figure 2 depicts XRD patterns of ZnO thin films where all diffraction peaks could be assigned to the hexagonal wurtzite structures with a $P6_3mc$ space group symmetry and Zn atoms in tetrahedral sites, which are in good agreement with the JCPDS Card No. 36-1451. All samples show no extra peaks due to impurity, which indicates ZnO with high purity of crystalline was obtained. It can be confirmed that the variation of different Zn salts did not affect the XRD peak intensity. However, zinc nitrate as salt precursor slightly shifted to lower angles compared to others. The shift in the peak position could be attributed to the increased lattice parameter, which later would induce lattice strain (tension) [15].

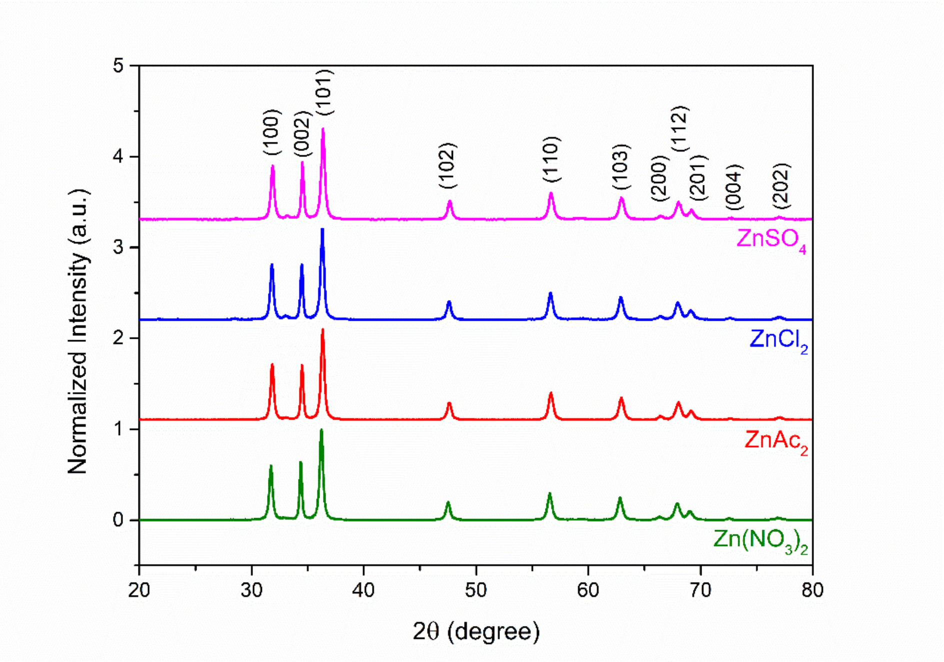


Figure 2: XRD spectra of ZnO thin films with different Zn salt precursors.

The surface morphology of the ZnO thin films is shown in Figure 3. All the FESEM images of ZnO ranged in size less than 500 nm and are distinguishable based on their morphologies and feature sizes. Figure 3(a) exhibits the nanorods structure, whereas (b) resembles a more flakes-like structure. In contrast, (c) displays a hollow-rod structure, while flower-like structures consisting of nanorods cluster are observed in (d). Different Zn salts used for the deposition result in different ZnO morphologies. The growth of ZnO structures easily occurs when a rougher surface that contains more vacancies can absorbs and receives more atoms, particles and nuclei, leading to more nucleation sites [9]. The particle distribution of ZnO on the glass substrate will determine the condensed state and compactness of the deposition. An increase in ZnO particles deposition can yield further surface roughness that would impact wettability [12].

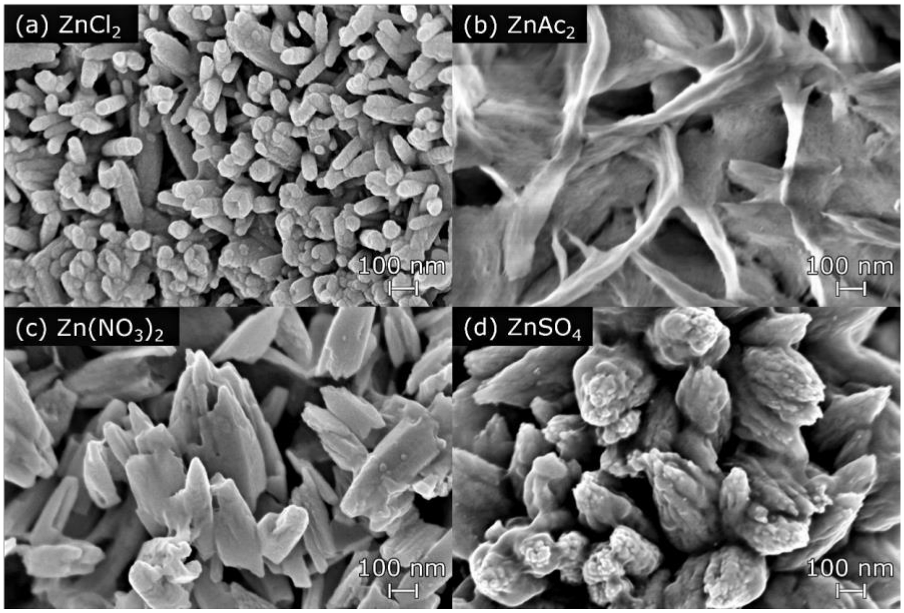
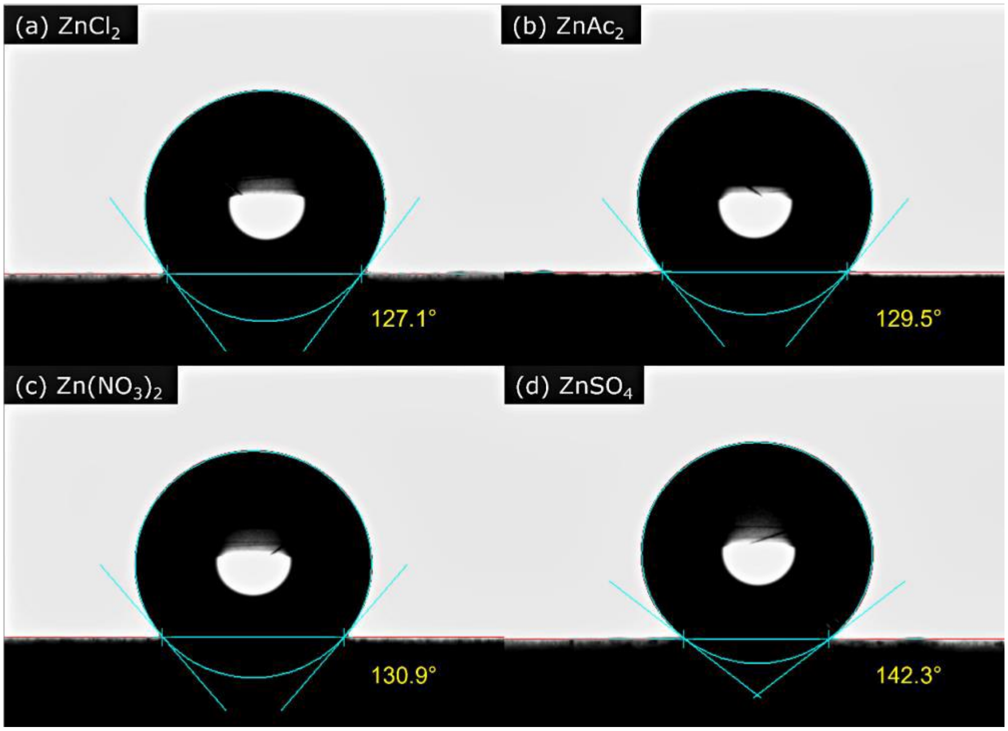


Figure 3: FESEM images of ZnO thin films with different Zn salt precursors with 70 kX magnification.

Figure 4 reveals photographs of water droplets on ZnO nanostructures grown on glass substrates. All samples demonstrate hydrophobic properties based on the CA measurement of the thin films carried out. The salt precursors have played a significant role in altering the morphology of the ZnO. It was shown that $ZnSO_4$ as a Zn source contributes to the highest CA of 142.3°. Coming next is $Zn(NO_3)_2$ with a CA value of 130.9°, followed by $ZnAc_2$ with a 129.5° CA value. Meanwhile, $ZnCl_2$ used as the Zn source show the lowest CA value of 127.1°. The highest interaction between the glass surface and water promotes the lowest CA values, which is in line with $ZnCl_2$. Also, reducing hydroxyl (−OH) groups at the surface lead to poor wettability of ZnO nanorods. On the other hand, $ZnSO_4$ hydrophobicity can be explained due to the air layers trapping between the nanorods cluster from the flower structures, consequently applying a resistive force against the preferred interfacial adhesion. For this reason, controllable hydrophobicity can be reached by manipulating the ZnO morphology and surface coverage density [16].

Two models are used to describe the surface wettability, the first represents the Wenzel model, and the latter refers to the Cassie and Baxter model. Both models imply that an increase in the surface roughness causes a substantial increase in CA. Although Cassie and Baxter's theory is better applied for a composite surface. They further added that air pockets trapped within its textured give significant rise to a CA value depending on the ratio of the element surface composition [13, 17].

Owing to the preferential growth of ZnO along the *c*-axis, the ZnO manifest a hydrophobic behaviour in aid of the dominant non-polar facets [13].



4. Conclusions

A simple and fast CBD protocol for fabricating ZnO nanostructured thin films was successfully grown on a permanganate-treated glass substrate. Tunable wettability was critically dependent on the morphological change coming from the selection of Zn salt precursor. Due to their morphology, the ZnO structures present different degrees of compactness, trapping air in-between. The film containing a higher volume of air trapped between the ZnO nanostructures at the solid interface has demonstrated more hydrophobic behaviour. In this case, $ZnSO_4$ as salt precursor results in the highest CA value (142.3°) among other Zn salts used.

Acknowledgements

We acknowledge this work was financially supported by a Fundamental Research Grant Scheme (FRGS) (FP064-2014A), SATU Grant (RU022F-2014) and Postgraduate Research Fund (PG228-2015A).

Conflicts of interest

The authors declare no conflict of interest.

References:

[1] F. Rahman, Zinc oxide light-emitting diodes: A review. *Optical Engineering*. 2019; 58: 010901-010921.

[2] M. Laurenti, V. Cauda, R. Gazia, M. Fontana, V.F. Rivera, S. Bianco, G. Canavese, Wettability control on ZnO nanowires driven by seed layer properties. *Eur. J. Inorg. Chem*. 2013; 14: 2520-2527.

[3] V. Khranovskyy, T. Ekblad, R. Yakimova, L. Hultman, Surface morphology effects on the light-controlled wettability of ZnO nanostructures. *Applied Surface Science*. 2012; 258: 8146– 8152.

[4] P. Yang, K. Wang, Z. Liang, W. Mai, C.-X. Wang, W. Xie, P. Liu, L. Zhang, X. Cai, S. Tan, J. Song, Enhanced wettability performance of ultrathin ZnO nanotubes by coupling morphology and size effects. *Nanoscale*. 2012; 4: 5755-5760.

[5] S. Shankar, J.-W. Rhim, Effect of Zn salts and hydrolyzing agents on the morphology and antibacterial activity of zinc oxide nanoparticles. *Environmental Chemistry Letters*. 2019; 17: 1105–1109.

[6] C.-H. Chao, P.-W. Chi, D.-H. Wei, Investigations on the crystallographic orientation induced surface morphology evolution of ZnO thin films and their wettability and conductivity. *The Journal of Physical Chemistry C*. 2016; 120: 8210-8219.

[7] H. Ennaceri, L. Wang, D. Erfurt, W. Riedel, G. Mangalgiri, A. Khaldoun, A.E. Kenz, A. Benyoussef, A. Ennaoui, Water-resistant surfaces using zinc oxide structured nanorod arrays with switchable wetting property. *Surface & Coatings Technology*. 2016; 299: 169-176.

[8] S. Duo, R. Zhong, Z. Liu, J. Wang, T. Liu, C. Huang, H. Wu, One-step hydrothermal synthesis of ZnO microflowers and their composition-/hollow nanorod-dependent wettability and photocatalytic property. *Journal of Physics and Chemistry of Solids*. 2018; 120: 20-33.

[9] B.-J. Lia, Li.-J. Huang, M. Zhou, N.-F. Ren, Morphology and wettability of ZnO nanostructures prepared by hydrothermal method on various buffer layers. *Applied Surface Science*. 2013; 286: 391-396.

[10] M. Shaban, M. Zayed, H. Hamdy, Nanostructured ZnO thin films for self-cleaning applications. *RSC Advances*. 2017; 7: 617-631

[11] T. Huhtamäki, X. Tian, J.T. Korhonen, R.H.A. Ras, Surface-wetting characterization using contact-angle measurements. *Nature Protocols*. 2018; 13: 1521-1538.

[12] T. Rezayi, M.H. Entezari, Wettability properties vary with different morphologies of ZnO nanoparticles deposited on glass and modified by stearic acid. *New Journal of Chemistry*. 2016; 40: 2582-2591.

[13] H. Ghannam, A. Chahboun, M. Turmine, Wettability of zinc oxide nanorod surfaces. *RSC Advances*. 2019; 9: 38289-38297.

[14] M.R.Y. Hamid, S.B.A. Hamid, B.H. Ong, The Effects of deposition time and seed layer on morphological properties of zinc oxide by chemical bath deposition. *Solid State Phenomena*. 2017; 264: 240-243.

[15] A.D. Prasetya, M. Rifai, Mujamilah, H. Miyamoto, X-ray diffraction (XRD) profile analysis of pure ECAP-annealing Nickel samples, *Journal of Physics: Conference Series*. 2020; 1436: 012113

[16] P.S. Emani, H.A. Maddah, A. Rangoonwala, S. Che, A. Prajapati, M.R. Singh, D.M. Gruen, V. Berry, S.K. Behura. Organophilicity of graphene oxide for enhanced wettability of ZnO nanorods. *ACS Applied Materials & Interfaces*. 2020; 12: 39772−39780.

[17] R. Mardosaitė, A. Jurkevičiū tė, S. Račkauskas, Superhydrophobic ZnO nanowires: Wettability mechanisms and functional applications. *Cryst. Growth Des*. 2021; 21: 4765-4779.