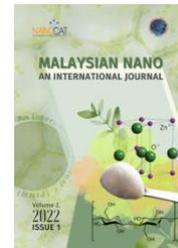




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Corresponding authors:
bhong@um.edu.my

Surface Wettability of ZnO Thin Films

M.R.Y Hamid ^a, A. Ma'amor ^b, B.H. Ong ^{a*}

Affiliations:

^aNanotechnology & Catalysis Research Centre (NANOCAT), Institute for Advanced Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia.

^bDepartment of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia.

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 (ZnCl₂), zinc acetate (ZnAc₂), zinc nitrate (Zn(NO₃)₂) and zinc sulfate (ZnSO₄). The crystallinity of ZnO thin films was evaluated using X-ray diffraction (XRD), and the surface morphology was observed using field emission scanning microscopy (FESEM). Finally, the wettability was determined by contact angle (CA) measurement. It was found that ZnCl₂ has the lowest CA (127.1°), while ZnSO₄ 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 $< 90^\circ$ are hydrophilic, while those with contact angles $\geq 90^\circ$ 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 (ZnCl₂), zinc acetate (ZnAc₂), zinc nitrate (Zn(NO₃)₂) and zinc sulfate (ZnSO₄) 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 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 scribe 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 (KMnO₄, Sigma-Aldrich), 99.8% *n*-butanol (C₄H₉OH, Merck), zinc chloride hexahydrate (ZnCl₂·6H₂O, Friendemann Schmidt), zinc acetate dihydrate (Zn(CH₃CO₂)₂·2H₂O, Merck), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Friendemann Schmidt), zinc sulfate heptahydrate (ZnSO₄·7H₂O, Sigma-Aldrich), ethanolamine (C₂H₇NO, Sigma-Aldrich) and ammonium hydroxide (NH₄OH, 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 KMnO₄ 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 K α radiation ($k = 1.5406 \text{ \AA}$) 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.

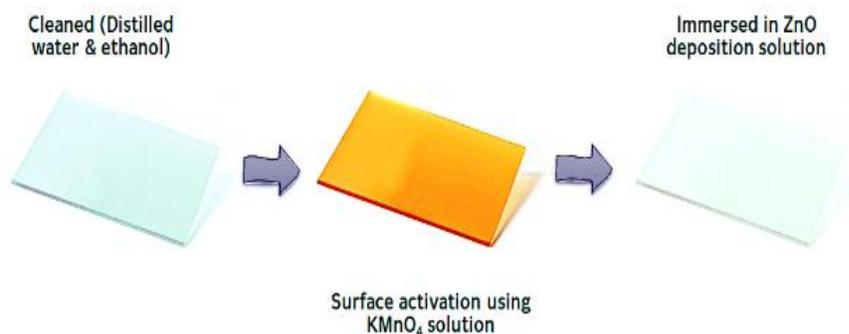


Figure 1: Schematic diagram of ZnO thin film fabrication using CBD method.

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].

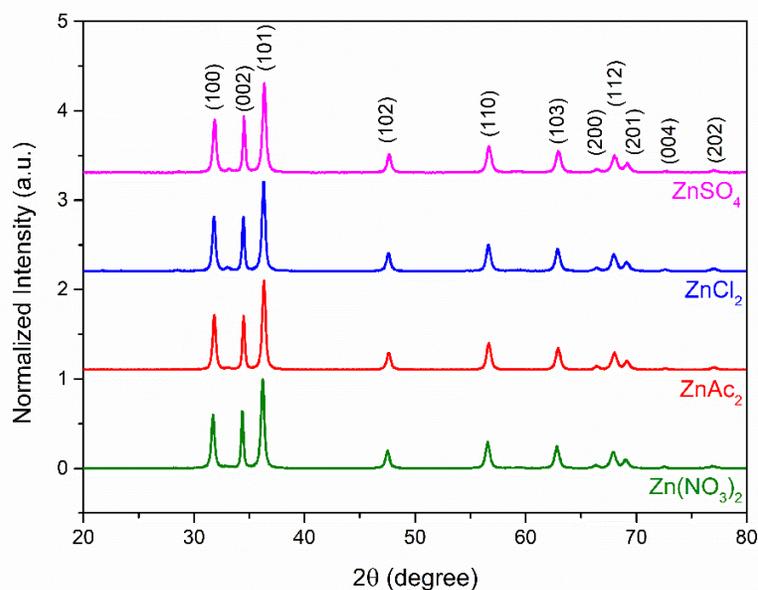


Figure 2: XRD spectra of ZnO thin films with different Zn salt precursors.

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 absorb and receive 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].

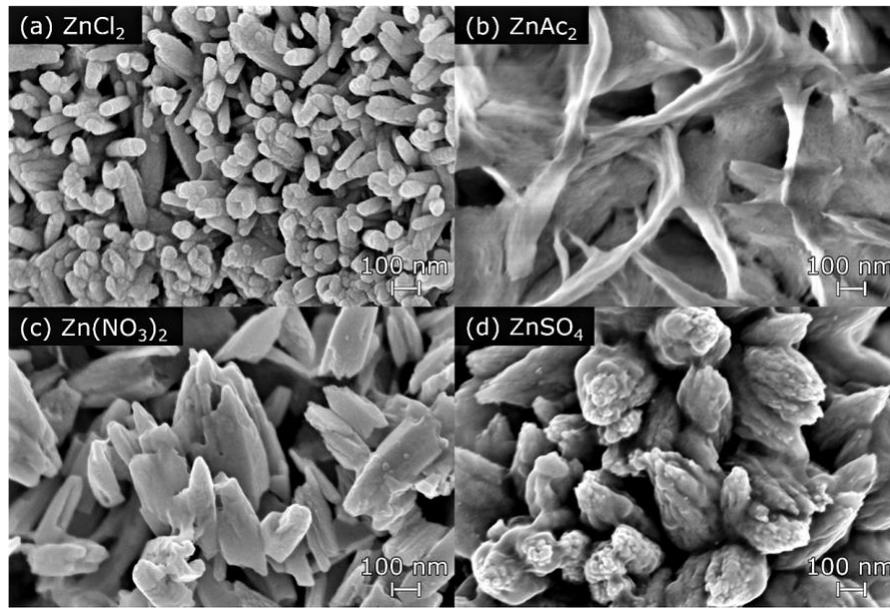
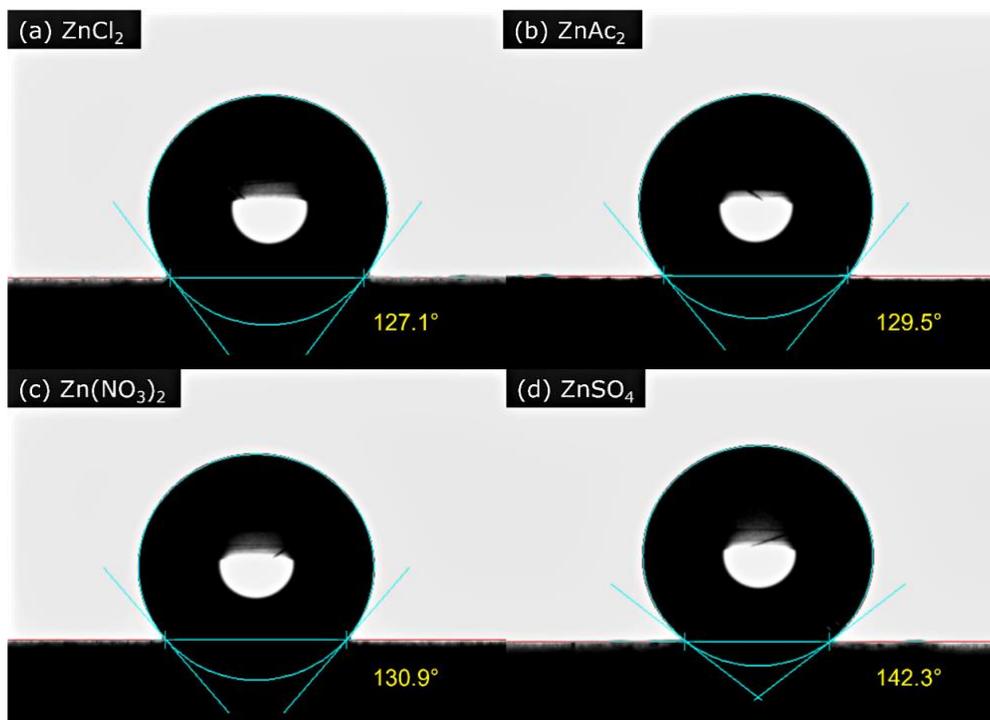


Figure 3: FESEM images of ZnO thin films with different Zn salt precursors with 70 kX magnification.

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 ZnSO₄ as a Zn source contributes to the highest CA of 142.3°. Coming next is Zn(NO₃)₂ with a CA value of 130.9°, followed by ZnAc₂ with a 129.5° CA value. Meanwhile, ZnCl₂ 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 ZnCl₂. Also, reducing hydroxyl (–OH) groups at the surface lead to poor wettability of ZnO nanorods. On the other hand, ZnSO₄ 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, ZnSO₄ as salt precursor results in the highest CA value (142.3°) among other Zn salts used.

Acknowledgements

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Conflicts of interest

The authors declare no conflict of interest.

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