Fabrication and Characterization of ZnO Thin Films by Sol-Gel Spin Coating Method for the Determination of Phosphate Buffer Saline Concentration

K.L. Foo1*, M. Kashif1, U. Hashim1 and M.E. Ali2

1Nano Biochip Research Group, Institute of Nano Electronic Engineering (INEE), Universiti Malaysia Perlis (UniMAP), 01000 Kangar, Perlis, Malaysia; 2Nanotechnology and Catalysis Research Centre, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Abstract: The fabrication, characterization and application of nanostructured zinc oxide (ZnO) thin films on interdigitated silver electrodes were described for the determination of phosphate buffer saline (PBS) concentration. The ZnO thin films were synthesized on a silicon dioxide wafer using a sol-gel spin coating technique. Two different seed solutions were prepared by dissolving Zn-acetate dihydrate in methanol and isopropanol in presence of a stabilizer, monoethanolamine. The field emission scanning electron microscope, atomic force microscope, X-ray diffractometer and Fourier transform infrared characterization revealed the presence of hexagonal ZnO nano-crystals in all thin films. However, the smaller sized and homogeneous ZnO nano-crystals were observed in isopropanol derived thin films. These thin films were used to discriminate the concentrations of different PBS solutions and the discriminatory signals were captured using a low-cost dielectric analyzer and a source meter. The frequency-capacitance curve reflected 2.85 fold increase in capacitance values when the sensor was exposed to 1000-fold diluted PBS in deionized water. A change in PBS concentration from 1000 fold to 10 fold increased the current flow from 6 μF to 122 μF. Thus the capacitance and current flow demonstrated a proportional relationship with the concentration of PBS, suggesting the application of the fabricated sensor in the determination and discrimination of chemical species concentration in various solutions.

Keywords: Interdigitated electrodes, Sol-gel spin coating technique, Dielectric analyzer and source meter, I-V curve, Double layer capacitance.

INTRODUCTION

Nanostructured ZnO has been intensively studied because of its useful semiconducting properties, broad band gap (3.2-3.37 eV), large excitation binding energy (60 meV) and high lattice constant. It has been successfully applied in biomedical sensors [1-2], chemical and gas sensors [3-4], ultraviolet light sensors [5-7], light-emitting diodes (LEDs) [8], solar cells [9-10] and other optoelectronic devices [11]. ZnO thin films are low dimensional nanostructured materials of great interests because of their unique physio-chemical properties [12-16] and convenient fabrication process into various types of nanostructures, such as nanowires (NWs) [1, 12], nanotubes [17], atomic force microscope, X-ray diffractometer and Fourier transform infrared characterization revealed the presence of hexagonal ZnO nano-crystals in all thin films. However, the smaller sized and homogeneous ZnO nano-crystals were observed in isopropanol derived thin films. These thin films were used to discriminate the concentrations of different PBS solutions and the discriminatory signals were captured using a low-cost dielectric analyzer and a source meter. The frequency-capacitance curve reflected 2.85 fold increase in capacitance values when the sensor was exposed to 1000-fold diluted PBS in deionized water. A change in PBS concentration from 1000 fold to 10 fold increased the current flow from 6 μF to 122 μF. Thus the capacitance and current flow demonstrated a proportional relationship with the concentration of PBS, suggesting the application of the fabricated sensor in the determination and discrimination of chemical species concentration in various solutions.

Keywords: Interdigitated electrodes, Sol-gel spin coating technique, Dielectric analyzer and source meter, I-V curve, Double layer capacitance.

EXPERIMENTAL

A p-type silicon wafer was ultrasonically cleaned into acetone and isopropanol (IPA). The unwanted native oxide layer on the wafer surface was removed through a buffer oxide etching (BOE). Finally, the silicon wafer was rinsed and cleaned with deionized (DI) water. Approximately 180-nm thick SiO2 layer was produced on the cleaved wafer surface using a wet oxidation process. A thermal evaporator was used to deposit a silver (Ag) layer on the SiO2/Si substrate for the interdigitated Ag electrodes (IDE) formation. Using a conventional lithography process, an IDE device of 8.75 mm X 5.00 mm in size was fabricated on the SiO2/Si substrate. In this work, an IDE with 10 fingers was used where the width and length of each finger was 0.25 mm and 3.75 mm, respectively, and the spacing between the two fingers was 0.25 mm.

Two types of ZnO seed solutions were prepared by dissolving zinc acetate dihydrate [Zn(CH3COO)2·2H2O] into methanol and IPA. To prepare 0.2M of ZnO seed solutions, 4.39 g of zinc acetate dihydrate was mixed in a 100 ml of methanol and a 100 ml of IPA solvents, respectively. The mixtures were vigorously stirred at 60°C for 30 min to completely dissolve the solute into the solvents. Subsequently, monoethanolamine (MEA) which was used as a stabilizer was added drop wise into the solution under constant stirring at 60°C for 2 h. Thus a transparent and homogenous solution was obtained. Prior to the deposition process, the solution was aged at room temperature for 24 h.

The aged ZnO solution was deposited onto the IDE device by using a low-cost spin coating technique at a speed of 3000 rpm for 20 s. The deposition process was repeated for 3 times to get a thicker ZnO thin film. For each deposition process, the coated ZnO thin films were dried at 150°C for 20 min to remove the organic residuals that might exist on the ZnO thin films. The coated ZnO thin films were then annealed in a furnace under ambient air at
500°C for 2h to get crystallized ZnO. The fabrication process flow is demonstrated in Fig. (1).

![Fig. (1). Process flow for the fabrication of IDE ZnO thin films on silicon wafer.](image)

The topography of the ZnO thin films were studied using FE-SEM and AFM. The XRD spectrum of sol-gel derived ZnO thin films were recorded at room temperature using an X-ray diffractometer. To confirm the chemical bonding and hexagonal wurtzite structure of the ZnO thin films, FTIR spectroscopy was performed. PBS with different concentrations was tested to show the application of the IDE ZnO thin films for the determination of chemical concentration, using a dielectric analyzer and a source meter.

**RESULTS AND DISCUSSION**

The surface morphology of ZnO thin films prepared from two different seed solutions (methanol and IPA) was studied using a FESEM and is given in Fig. (2). The results demonstrated that both solutions resulted in ZnO particles with hexagonal morphology. Although, the size of the nanoparticles in both cases were within the nanometer scale (<100 nm), the IPA solution produced smaller sized-grains (Scheme (b), Fig. (2)) than those obtained from methanol solution (Scheme (a), Fig. (2)). Additionally, the IPA derived ZnO particles were more uniformly distributed than those from methanol. Clear agglomerations of the nanoparticles were observed in certain areas of the methanol derived thin films, demonstrating their heterogeneity. The 3-D view of deposited ZnO thin films were studied using an AFM and is shown in Fig (3). The AFM image reflected nanometer scale ZnO crystals in both thin films. However, the IPA derived thin films (~100 nm) were thicker than those from methanol (~40 nm) derived one.

An X-ray diffraction analysis was carried out to study the crystal quality and orientation of the synthesized ZnO thin films Fig (4). All diffraction peaks in XRD spectra were matched with the reference spectra (JCPDS 36-1451) of standard ZnO, demonstrating the formation ZnO crystals. The sharp and narrow diffraction of the peaks demonstrated that all ZnO thin films were of good crystalline in quality [29]. The reflection peaks at (100), (002), (101), (110), (103) and (112) were indicative of the hexagonal wurtzite ZnO nano-structure [30]. The crystal growth orientation of ZnO thin films obtained from methanol solvent produced the highest peak at 34.56°, which was on (002) plane. However, the IPA-derived ZnO thin films provided the highest diffraction peak at 36.36°, which was on (101) plane. Thus both planes demonstrated the pure hexagonal wurtzite ZnO structure in the fabricated thin films[31]. The XRD results also reflected that methanol and IPA derived ZnO crystals had different morphology and crystal growth orientation supporting the FESEM findings.

The chemical bonding, compositional quality and functionalities of ZnO thin film were studied using FTIR spectroscopy. The FTIR spectra obtained in the range of 400-4000 cm⁻¹ is shown in Fig (5). The stretching vibration of Zn-O bond was reflected by a peak at 458 cm⁻¹ [31]. These absorption spectra also showed that the fabricated thin films were composed of hexagonal wurtzite ZnO structure, strongly supporting the FESEM and XRD findings. The broad band at 611 cm⁻¹ was due to the existence of the local vibration of the substituted carbon in the Si crystal lattice[32]. The broad band observed at 812 cm⁻¹ was assigned to the C-H mode vibration. Whereas the sharpest peak at 1092 cm⁻¹ was assigned to the stretching frequency of Si-O bond [33].

Finally, the ability of the IDE ZnO thin film to differentiate different chemical concentrations was verified using a dielectric analyzer. The test was performed in the frequency range of 1Hz to 1MHz with applied AC voltage of 1V in presence of air, DI water and PBS buffer of different concentrations. The measurement showed the minimum or null effect of double layer occurrence in the IDE ZnO thin films. The capacitance-frequency (C-F) curve is demonstrated in Fig (6). The lowest value of capacitance was observed when the device was tested under air environment. This phenomenon was probably due to the charge carrier density in the ZnO thin films, since very little or no charge is contributed by air under normal circumstances [34]. However, when the device was tested with water, a slight change (2.8uF) in capacitance was found. The changes in capacitance became more prominent when different PBS solutions were applied on the ZnO thin film device. The capacitance increased dramatically with the increment of the PBS solution concentration from 1000:1 to 10:1 in DI water. The respective capacitance values were 6uF and 122uF, indicating a change in
Fig. (3). 3-D view of ZnO thin films deposited from (a) methanol and (b) IPA.

Fig. (4). X-ray diffraction patterns of ZnO thin films derived from (a) methanol and (b) IPA dissolved Zn-acetate solutions.

Fig. (5). FTIR spectra of ZnO thin films derived from methanol (blue line) and IPA (red line) dissolved Zn-acetate solutions.

Fig. (6). Capacitance of IDE ZnO thin films under various conditions as shown in the inset; DIW and PBS denote deionized water and phosphate buffer saline.

Fig. (7). Current-voltage curve with DIW and different PBS concentration.
capacitance values by 20.33 fold. This phenomenon was due to the smaller thickness of double layer when the device was exposed to the higher concentration of the PBS solutions [35]. Therefore, the electric potential was dropped in the smaller size of gap between the IDE fingers, resulting in higher capacitance in the IDE ZnO thin films [36].

To have a current-voltage (I-V) curve for various concentration of PBS, an IDE ZnO thin film was connected to the Keithley 2400 source meter and the measurements were done under atmospheric conditions with an applied voltage of 0-2V. Due to the limitations in source meter current, it was not possible to test the fabricated device under air atmosphere, a study that was conducted during C-F measurements. The ZnO thin films showed the lowest current flow (13.6 μA, 2V) when DI water was dropped on it Fig (7). This was due to the higher resistance of DI water (18.2MΩ) which has very little ion flow that resulted in little ion carrier in the ZnO thin films. The current flow in ZnO thin film increased when the device was tested in PBS solutions. The measured current flow of the device at 2V in 1000-, 100- and 10-fold diluted PBS saline was 69.3μA, 422μA and 3mA, respectively. Since the current was increased with an increase in concentration of PBS buffer, it was assumed that the device could be used in chemical sensing devices to determine the chemical concentration. The trend indicated that more ion flows through the IDE gaps in ZnO thin films with the increase in PBS buffer concentration. This phenomenon was in agreement with the concept of Ohm’s law [37].

CONCLUSION
Nanostructured ZnO thin films were synthesized on interdigitated silver electrodes grown on SiO₂/Si substrates using a sol-gel method. The seed solutions were prepared by dissolving Zn-acetate dihydrate in methanol and isopropanol in presence of monoethanolamine as a stabilizer. The FESEM, XRD, AFM and FTIR characterization revealed that the thin films were composed of hexagonal ZnO nano-crystals with c-axis orientation. However, the IPA derived thin films were more homogeneous and were composed of smaller sized ZnO crystals. The IPA derived IDE ZnO thin films were used to determine the concentration of different PBS buffer using a low cost dielectric analyzer and source meter. An increment in capacitance and current flow was observed with the increment in the concentration of PBS solutions, suggesting the applications of such devices in the determination of chemical concentration.

CONFLICT OF INTEREST
The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS
The authors wish to acknowledge the financial support of the Malaysian Ministry of Higher Education (MOHE) through the FRGS grant no. 9003-00276 to Prof. Dr. Uda Hashim. The authors would also acknowledge the technical contributions from the staffs of Institute of Nano Electronic Engineering and School of Microelectronic Engineering in the University Malaysia Perlis to smoothly perform this research.

REFERENCES


