Experimental evaluation of ZnO nanowire array based dynamic pressure sensor

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Abstract

This paper presents the synthesis of ZnO nanowire array on metallic alloy substrate, its packaging and experimental evaluation for dynamic pressure sensing applications. Vertically aligned dense nanowire array was synthesized using hydrothermal method. Crystal structure, morphology and chemical composition analysis were carried out using X-ray diffraction, field emission scanning electron microscopy and energy dispersive spectroscopy respectively. ZnO nanowires were grown to an average height of 2.2 μm with an average diameter of 200 nm. The as-synthesised nanowire array was packaged as a pressure sensor and was evaluated for its sensing properties. The sensor responded to shock pressure input with a sensitivity 1.65 ± 0.15 mV/bar, rise time 1.38 ms and discharge time 1.79 ms. ZnO nanowire array demonstrated highly promising features which are desirable for a dynamic pressure sensor.

Keywords ZnO · Nanowire · Hydrothermal · Parylene-C · Dynamic pressure · Shock tube

1 Introduction

ZnO is a group II–VI binary compound semiconductor which exhibits piezoelectric properties. ZnO attracted researchers in the recent past due to various advantages such as biocompatibility, chemical & thermal stability, suitability for harsh environment, diversified device application, affordability and abundance in nature [1–3]. ZnO is a key technological material finding wide applications in electronics, biomedical, optics, sensors, cosmetics, photonics etc. Though studies were conducted on its bulk and thin film forms in the past, the current research thrust is on its nanoforms. A wide variety of nanostructures in 1D & 2D forms can be synthesised using ZnO, such as nanorods [4], nanowires [5], nanorings [6], nanoribbons/nanobelts [7], nanotubes [6], nanospheres [8], nanoflowers [9], nanosheets [10] etc. Among the 1D nanostructures, ZnO nanorods/nanowires have been studied because of their

easy formation and device application [4]. Some of the applications of ZnO nanowires reported in literature are energy source [1], hydrogen gas sensor [11], oxygen gas sensor [12], biosensor [13], pressure & temperature sensor [14], tactile sensor [15], photodiodes [3], photocatalyst [16], solar cell [17], light emitting diode [13], UV lasers [18], field effect transistors [13] etc.

ZnO nanostructures with tailor-made properties can be fabricated using controlled synthesis approaches. Various bottom up approaches like chemical bath deposition (CBD) [2, 13–16], electrodeposition [19, 20], vapour liquid solid (VLS) method [1, 3–5], chemical vapour deposition (CVD) [2, 4, 11, 13] and physical vapour deposition (PVD) [13] are reported in literature for the synthesis of ZnO nanowires. Vapour phase growth methods (VLS, CVD & PVD) are complex due to the requirement of high vacuum and high temperature. However, chemical solution based methods like CBD and electrodeposition are found to be

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cost effective and simple. CBD methods provide low cost fabrication of nanostructures on large wafers and do not require vacuum or high temperature.

Extensive studies have been carried out in the recent past regarding the synthesis of ZnO nanostructures and their potential applications. Nevertheless, the commercial deployment continues to be in infancy stage due to the challenges in manufacturing processes, packaging techniques etc. [21]. Our research work has elicited very promising results in addressing the above bottlenecks. We have synthesised ZnO nanowire array using a simple and cost effective hydrothermal method. As-synthesised nanowire array was packaged as pressure sensor and the sensor parameters such as sensitivity, rise time and discharge time were evaluated. This paper reports the new and original results of ZnO nanowire synthesis, packaging and sensor characterisation, thereby confirming the commercial viability as a dynamic pressure sensor.

2 Experimental

2.1 Synthesis of nanowire array

As the current study focuses on evaluation of ZnO nanowire for dynamic pressure sensing application, a highly rugged and elastic substrate is required. Hence, a material called phynox was chosen for substrate. Phynox is an alloy of Chromium, Cobalt and Nickel with properties such as high strength, high elasticity, wide temperature range etc. Phynox foil of thickness 50 μm , cut into 12 mm diameter circular piece was used as substrate.

The substrate was thoroughly cleaned by ultrasonic agitation in industrial grade soap solution, acetone and isopropyl alcohol sequentially to remove organic and inorganic impurities. Substrate was then washed using de-ionised water and dried. The cleaned substrate was masked using kapton tape for an area of 2 mm $\times$ 2 mm for bottom electrode contact. ZnO seed layer of 100 nm thick

was deposited on the substrate using RF reactive magnetron sputtering method. Deposition was carried out at room temperature for a duration of 10 min under a working pressure of 1.4×10^{-2} mbar, RF power 120 W, target—substrate distance 28 cm, Ar–O₂ ratio 85–15%. Nanowire synthesis was initiated after annealing the seed layer at 300 °C in a hot air oven for 1 h.

Equimolar concentration (25 mM) solutions of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethelene tetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$) were prepared. Then, the solutions were mixed and stirred using magnetic stirrer for 5 min. From the mixture, 50 ml was taken in glass bottle. The substrate with ZnO seed layer was placed over the surface of the solution with seed layer touching the solution. The glass bottle was closed and kept at 85 °C inside hot air oven. After 5 h, oven temperature was brought down to room temperature and substrate with ZnO nanowire array was removed from glass bottle. It was cleaned thoroughly with DI water and dried at room temperature. Figure 1 shows the schematic of various processes involved in the synthesis of ZnO nanowire array.

The as-synthesised ZnO nanowire array was characterized using X-ray diffraction (XRD) for crystal structure, field emission scanning electron microscopy (FE-SEM) for morphology and energy dispersive spectroscopy (EDS) for chemical composition. The equipment used were Bruker D8 advance diffractometer for XRD, Carl Zeiss model No: Ultra 55 for SEM and Oxford INCA for EDS.

2.2 Packaging and testing of ZnO nanowire array based sensor

In order to provide robustness, moisture protection and isolation between top and bottom electrodes, the as-grown nanowires on phynox substrate was coated with a layer of parylene-C to a thickness of 2 μm . The bottom electrode contact point was masked using kapton tape during parylene-C coating also. Parylene-C is a piezoelectric polymer material used as conformal coating for

Fig. 1 Schematic of nanowire synthesis process

devices used in medical, defense, aerospace and electronics industries [22, 23]. Properties such as piezoelectric effect, non-conductivity, chemical inertness, bio compatibility, high mechanical & dielectric strength etc. are the key factors for selecting the material for the present work. Since the parylene-C layer is very thin, it will not hinder the flexibility of the nanowire for bending on application of pressure.

The substrate being a conducting material, was directly used as bottom electrode. A fine layer of silver epoxy paint applied over the parylene-C coating was used as

top electrode. Copper lead wires of 70 μm diameter were attached to the electrodes using silver epoxy paste. Figure 2 shows the schematic of parylene-C coated ZnO nanowire array with lead wires.

ZnO nanowire array with lead wires was bonded on a deflecting membrane (diaphragm) of 14 mm diameter and 0.380 mm thickness, designed to withstand a peak pressure of about 20 bar. The diaphragm was fabricated using steel of high mechanical strength and elastic properties and was welded to a pressure port having suitable mounting thread. Figure 3a shows the schematic of fully

Fig. 2 Schematic of parylene-C coated ZnO nanowire array with electrical leads

Fig. 3 **a** Schematic of packaged ZnO nanowire array based sensor, **b** photograph of the packaged sensor

packaged ZnO nanowire array based dynamic pressure sensor with electrical and mechanical interface and Fig. 3b shows the corresponding photograph.

Figure 4 shows the working principle of the ZnO nanowire array based pressure sensor. When pressure is not applied, ZnO nanowires are not strained and will be vertical to the substrate as shown in Fig. 4a. However, when pressure is applied, the diaphragm and hence the substrate get deflected as in Fig. 4b, transferring the strain to nanowires. As a result, the ZnO nanowires get deformed leading to the generation of piezoelectric voltage.

The packaged sensor was evaluated for dynamic pressure sensing properties by using a shock tube. A shock tube can be used for generating shock waves with rise time of the order of few nanoseconds and peak amplitude ranging from few bar to more than 100 bar [24, 25]. Shock tube is considered as a standard for dynamic pressure calibration in metrology [24, 25]. Shock tube consists of driver section and driven section, separated from each other by a membrane. Driver section is connected to a N₂ cylinder. When the pressure inside the driver section is increased by opening the N₂ cylinder, the membrane bursts and generates shock waves. Testing of the sensor was carried out in comparison with an industrial standard piezoelectric quartz type reference sensor of Make: PCB Piezotronics, Model No: 113B22, sensitivity 14.4 mV/bar. The sensor under test and reference sensor were mounted on the end flange of the shock tube. Output of both sensors were connected to a storage oscilloscope. Figure 5 shows the schematic of the test setup used for the evaluation of ZnO nanowire array sensor. Pressure waves of required amplitude were generated in the shock tube by using polycarbonate sheets of varying thickness as membrane material.

3 Results and discussion

3.1 Material characterisation

Figure 6 shows the XRD pattern of the ZnO nanowires grown on phynox substrate. The sharp diffraction peak at about 34° indicates high degree of crystalline nature of as-grown nanowires which are highly vertically oriented. Other two peaks correspond to Chromium and Cobalt from the substrate. Morphology of the as-synthesised nanowire array as indicated by the FE-SEM is shown in Fig. 7. The cross section shown in Fig. 7a confirms that ZnO nanowires are well aligned and grown vertical to the substrate surface with almost uniform length and diameter. Topography of the ZnO nanowire array shown in Fig. 7b shows formation of thickly populated nanowires. The as-grown nanowires are having hexagonal tips as shown in inset of Fig. 7b indicating the wurtzite structure of ZnO single crystal. The FE-SEM measured an average diameter of 200 nm and average height of about 2.2 µm for ZnO nanowires. The SEM images of ZnO nanowire array after parylene-C coating is shown in Fig. 8a, b. Nanowires are completely embedded within parylene-C forming a perfect conformal coating for the nanowire array. The EDS spectra of ZnO nanowire array shown in Fig. 9 indicates the presence of Zn and O atoms.

3.2 Evaluation of ZnO nanowire sensor

The packaged sensor and reference sensor were mounted on the end flange of the shock tube. Pressure inside the driver section was increased by releasing N₂ gas from the

Fig. 4 Working principle of ZnO Nanowire array based pressure sensor **a** sensor when pressure is not applied, **b** sensor when pressure is applied

Fig. 5 Schematic of the shock tube test setup

Fig. 6 XRD pattern of the as-grown ZnO nanowire array

cylinder using a regulator till the membrane burst. As a result, shockwaves were generated in the driven section of the shock tube. The shock waves exert pressure on the sensors leading to the generation of piezoelectric voltage. Output signals from both sensors were acquired using storage oscilloscope. Test was conducted for 5 different shock pressure levels 6.52 bar, 8.61 bar, 12.01 bar, 14.03 bar and 17.22 bar. Figure 10 shows piezoelectric response of the sensors to shock wave signal of 17.22 bar pressure (first peak) where the peak output of the reference sensor was 0.248 V and that of ZnO nanowire sensor was 0.0308 V. The subsequent peaks are due to reflected shock waves. Figure 11 shows the output plot of ZnO nanowire array based sensor for different shock pressure

Fig. 7 FE-SEM image of the as-grown ZnO nanowire array **a** cross-section, **b** topography. The inset shows highly magnified image

Fig. 8 FE-SEM image of the ZnO nanowire array after parylene-C coating **a** cross-section, **b** topography

Fig. 9 EDS spectra of the as-grown ZnO nanowire array

Fig. 10 Response of hydrothermally grown ZnO nanowire array based dynamic pressure sensor & reference sensor to shockwave (17.22 bar pressure)

Fig. 11 Output of ZnO nanowire sensor for different shock pressure levels

levels. Average sensitivity of the sensor was computed as 1.65 ± 0.15 mV/bar. From Fig. 10, it is clear that the rise time (time taken to reach 10% to 90% of the peak value) and discharge time (time taken to discharge to 37% of the peak) of ZnO nanowire based sensor are comparable with the reference sensor. Rise time and discharge time are computed as 1.38 ms ($T_2 - T_1$) as in Fig. 12a and 1.79 ms

($T_4 - T_3$) as in Fig. 12b respectively. Though the sensitivity is less compared to the quartz based reference sensor, hydrothermally grown ZnO nanowire array based sensor demonstrated highly promising properties such as sharp output peaks, fast rise time and discharge time making it highly suitable for dynamic pressure sensing applications.

4 Conclusion

ZnO nanowires were grown on phynox substrate using hydrothermal method. Crystal structure, morphology and chemical composition of the as-grown nanowires were characterised using XRD, FE-SEM and EDS respectively. SEM indicated formation of vertically aligned dense nanowire array with average diameter of 200 nm and average height of 2.2 μ m for the nanowires. The packaged ZnO nanowire array based sensor produced piezoelectric output voltage with a sensitivity of 1.65 ± 0.15 mV/bar. The rise time and discharge time of the sensor were computed as 1.38 ms and 1.79 ms respectively. The present work successfully demonstrated the suitability of hydrothermally synthesised ZnO nanowire array for dynamic pressure sensing applications.

Fig. 12 Evaluation of **a** rise time ($T_2 - T_1 = 1.38$ ms), **b** discharge time ($T_4 - T_3 = 1.79$ ms)

Compliance with ethical standards

Conflicts of interest On behalf of co-authors, I assure that there is no conflicts of interest between the authors.

References

- Wang ZL, Song J (2006) Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science* 312:242–246
- Wallace I (2015) Synthesis and characterisation of zinc oxide (ZnO) nanowire. *J Nanomed Nanotechnol* 6(5):1–9
- Luo L, Zhang Y, Mao SS, Lin L (2006) Fabrication and characterization of ZnO nanowires based UV photodiodes. *Sens Actuators, A* 127:201–206
- Yi G-C, Wang C, Park WI (2005) ZnO nanorods: synthesis, characterisation and applications. *Semicond Sci Technol* 20(4):S21–S34
- Riaz M, Song J, Nur O, Wang ZL, Willander M (2010) Study of the piezoelectric power generation of ZnO nanowire arrays grown by different methods. *Adv Funct Mater* 11:1–6
- Zhang S-L, Byun H-G, Lim J-O, Huh J-S, Lee W (2012) Controlled synthesis of ZnO nanostructures for sub-ppm-level VOC detection. *IEEE Sens J* 12(11):3149–3155
- Zhao M-H, Wang Z-L, Mao SX (2004) Piezoelectric characterisation of individual zinc oxide nanobelt probed by piezoresponse force microscope. *Nano Lett* 4(4):587–590
- Karthikeyan L, Akshaya MV, Basu PK (2017) Microwave assisted synthesis of ZnO and Pd-ZnO nanospheres for UV photodetectors. *Sens Actuators, A* 264:90–95
- Mao Z, Du L, Hu D, Wang Y, Yu N (2012) Synthesis of ZnO nanoflower arrays on patterned sapphire by aqueous solutions. In: *IEEE international conference on optoelectronics and microelectronics*, pp 397–399
- Modaresinezhad E (2015) Realization of self-bias humidity sensor, based on ZnO nanosheets. In: *23rd Iranian conference on electrical engineering (ICEE)*, pp 1149–1153
- Lupan O, Emelchenko GA, Ursaki VV, Chai G, Redkin AN, Grunzintsev AN, Tiginyanu IM, Chow L, Ono LK, Roldan Cuenya B, Heinrich H, Yakimov EE (2010) Synthesis and characterisation of ZnO nanowires for nanosensor applications. *Material Res Bull* 45:1026–1032
- Lu CY, Chang SP, Chang SJ (2008) ZnO nanowire based oxygen gas sensor. In: *IEEE international conference on electron devices and solid state circuits*, pp 1–4
- Zhang Y, Ram MK, Stefanakos EK, Yogi Goswami D (2012) Synthesis, characterization and applications of ZnO nanowires. *J Nanomater* 2012:1–22
- Lee KH, Sim M, Ryu M, Shin JH, Jang JE, Sohn JI, Cha SN (2015) Zinc oxide nanowire based pressure and temperature sensor. In: *Proceedings of the 15th IEEE international conference on nanotechnology*, pp 901–904
- Sim M, Lee K, Jeong Y, Shin JH, Sohn JI, Cha SN, Jang JE (2016) Structural Solution to enhance the sensitivity of a self-powered pressure sensor for an artificial tactile system. *IEEE Trans Nano-Bio Sci* 15(8):804–811
- Zhou Q, Wen JZ, Zhao P, Anderson WA (2017) Synthesis of vertically—aligned zinc oxide nanowires and their application as photocatalyst. *Nanomaterials* 7(9):1–6
- Yang W, Wan F, Chen S, Jiang C (2009) Hydrothermal growth and application of ZnO Nanowire Films with ZnO and TiO₂ buffer layers in dye-sensitized solar cells. *Nanoscale Res Lett* 4(1):1486–1492
- Chu S, Wang G, Zhou W, Lin Y, Chernyak L, Zhao J, Kong J, Li L, Ken J, Liu J (2011) Electrically pumped waveguide lasing from ZnO nanowires. *Nat Nanotechnol* 6(8):506–510
- Willander M (2014) Zinc oxide nanostructures—advances & applications. Pan Stanford Publishing Pte Ltd, Singapore
- Orlov A, Ulianova V, Yakimenko Y, Bogdan O, Pashkevich G (2013) Synthesis of ZnO nanorods for acoustic wave sensor. In: *IEEE XXXIII international scientific conference electronics and nanotechnology (ELNANO)*, pp 25–27
- Hu Y, Wang ZL (2015) Recent progress in piezoelectric nanogenerators as a sustainable power source in self-powered systems and active sensors. *Nano Energy* 14:1–12
- Kim JY-H, Liu Y, Scianmarello N, Tai YC (2013) Piezoelectric parylene-C MEMS microphone. In: *17th IEEE international conference on transducers & eurosensors*, pp 39–42
- Kim JY-H, Cheng A, Tai YC (2011) Parylene-C as a piezoelectric material. In: *24th IEEE international conference on micro electro mechanical systems*, pp 473–476
- Wang Z, Li Q, Wang Z, Yan H (2015) Novel method for processing the dynamic calibration signal of pressure sensor. *Sensors* 15:17748–17766
- Downes S, Knott A, Robinson I (2014) Towards a shock tube method for the dynamic calibration of pressure sensors. *Philos Trans R Soc A* 372(2023):1–17

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