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# Fabrication and Characterization of Room Temperature Hydrogen Gas Sensor Using ZnO Nanocrystalline Fibers Prepared by Electrospinning

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**ABSTRACT.** Room temperature hydrogen gas sensor was successfully fabricated using ZnO nanocrystalline fibers prepared by electrospinning a precursor mixture of polyvinylpyrrolidone (PVP) and zinc acetate, followed by annealing at 500 °C for 4 hours in air. The ZnO nanocrystalline fibers were characterized by X-Ray Diffraction (XRD) which indicated that the fibers are single phase nanocrystalline ZnO. Surface morphology and chemical composition of ZnO nanocrystalline fibers were studied by Field Emission Scanning Electron Microscopy (FESEM) equipped with EDS spectroscopy. The sensitivity of the sensor towards hydrogen gas was about 4.9% in 2000 ppm.

***Keywords:*** *Hydrogen gas sensor, Electrospinning, ZnO;*

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## 1. INTRODUCTION

As one of II-VI compounds, Zinc oxide (ZnO) has a wide energy band gap of 3.37 eV, and large exciton binding energy of 60 meV. It has a hexagonal wurtzite-type structure and is non-toxic and relatively cheap. ZnO in one-dimensional (1-D) nanostructures offer extra characteristics such as high aspect ratios, high electron mobility and possess both electrical and optical anisotropy [1,2]. These unique multiple characteristics make ZnO suitable for various applications including solar cell [3], gas sensor [4] and photodetector [5]. There are various methods reported in fabricating 1-D ZnO such as sol-gel, electrodeposition, solvothermal routes, vapor-solid, vapor-liquid-solid, solution-solid and electrospinning. Electrospinning is one of the simple and versatile methods among others. It is a method of producing fiber from polymer solutions with diameter ranging from nano to micro scale [6].

In this work, ZnO nanocrystalline fibers prepared by electrospinning were used to fabricate $H_2$ gas sensor. The main aim of this work is to demonstrate the sensing capability of ZnO nanocrystalline fibers toward $H_2$ gas at room temperature.

## 2. MATERIALS AND METHOD

1.5 M $Zn(CH_3COO)_2.2H_2O$ was mixed with 10% PVP dissolved in ethanol with a volume ratio of 1:9 was used for electrospinning. The mixture was stirred for 1 hour and sonicated to remove any bubbles trapped in the solution. The solution was then loaded into a plastic syringe and connected to a high voltage power

supply. A voltage of 16 kV was applied between the collector and the syringe separated at a distance of 16 cm. The solution flow rate was maintained at 0.03 ml/min.

A rotating steel wire drum was used as nanofibers collector. Fig. 1 shows the electrospinning setup. The fibers were transferred to $SiO_2$ coated Si wafers and annealing was performed in air at temperature of 500 °C for 4 hours to remove the organic constituents of the fibers and to obtain nanocrystalline ZnO phase. A Netzsch STA-449-F3 Jupiter was used for simultaneous TG-DSC analysis. Nitrogen gas with a constant flow rate of 20 ml/min and a heating rate of 10 °C/min was used in the analysis. Both the structures of PVP/zinc acetate and ZnO nanofibers were characterized by X-ray diffraction (XRD) using PANAlytical XPert Pro MPD with Cu Kα irradiation. The morphologies of the nanofibers were examined by field emission scanning electron microscope (FESEM) Carl Zeiss GeminiSEM 500 equipped with an Oxford X-Max EDS detector.

Gas sensing tests were performed with gas flowing across the sensor chip in a sealed small acrylic glass chamber. Hydrogen was diluted at various proportions with dry air and the flow rates were regulated by mass flow controllers at 200 SCCM. Gas sensing data was acquired via a customized Labview program interfaced with a Keithley Series 2600B. A constant voltage of 1.4 V was applied. All experiments were carried out with the sensor chip first exposed to air to obtain the baseline resistance, followed by exposure to the desired concentrations of hydrogen gas before the air was flushed back to complete a cycle.

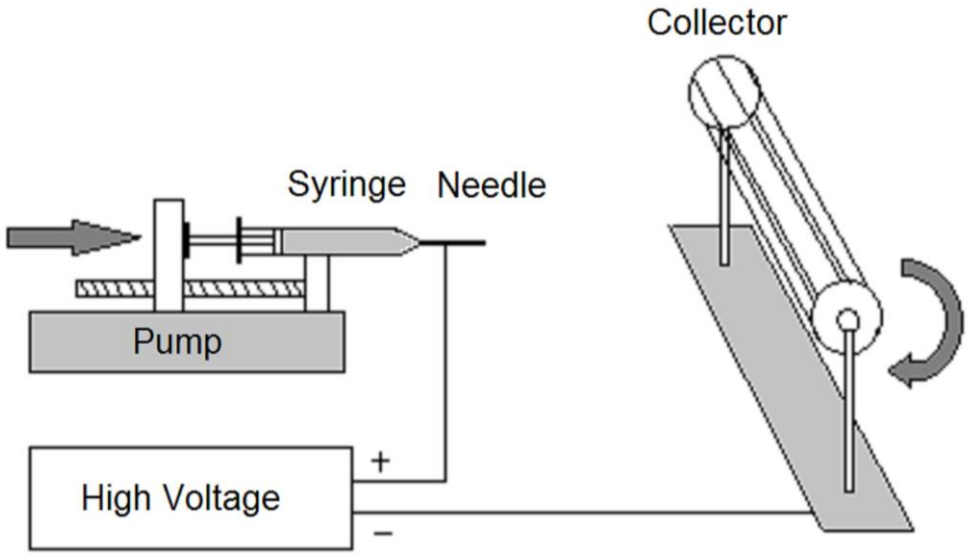


**Fig. 1** Schematic diagram of the electrospinning setup

## 3. RESULTS AND DISCUSSION

TG and DSC curves of PVP/zinc acetate fibers at $N_2$ atmosphere with temperature range RT-900 °C are shown in Fig. 2. The weight losses (~56%) found from TGA curves agree well with those estimated to the decomposition of PVP and zinc acetate and the formation of oxide. The TGA curve of PVP/zinc acetate fibers indicated three stages of decomposition. The first weight loss at around room temperature to 140 °C is attributed to the liberation of a small amount of water moisture. The second weight loss happens at around 220-320 °C due to loss of water of crystallization and melting of the polymer. The third stage is observed in a

range of 340-480 °C, which corresponds to the decomposition of organic phase. This was confirmed by the sharp exothermic peak observed in the DSC curve at about 460 °C. When the temperature reaches about 500 °C, the curve becomes flat which indicates that the PVP/zinc acetate fibers has completely transformed into inorganic oxide fibers. A broad exothermic peak appears between 520 and 900 °C, which probably due to ZnO crystals growth. In our previous work [7], results showed that calcination at 500 °C can maintain the

structure of fiber while the fibers developed into segmented or dendritic structures after calcined at higher temperatures. The effect of applied voltage and calcination temperature on the morphology and diameters of the electrospun PVP/zinc acetate fibers has been investigated in the previous work also. Based on these findings, 500 °C was chosen as the annealing temperature to obtain nanocrystalline ZnO fibers for $H_2$ gas sensing application.

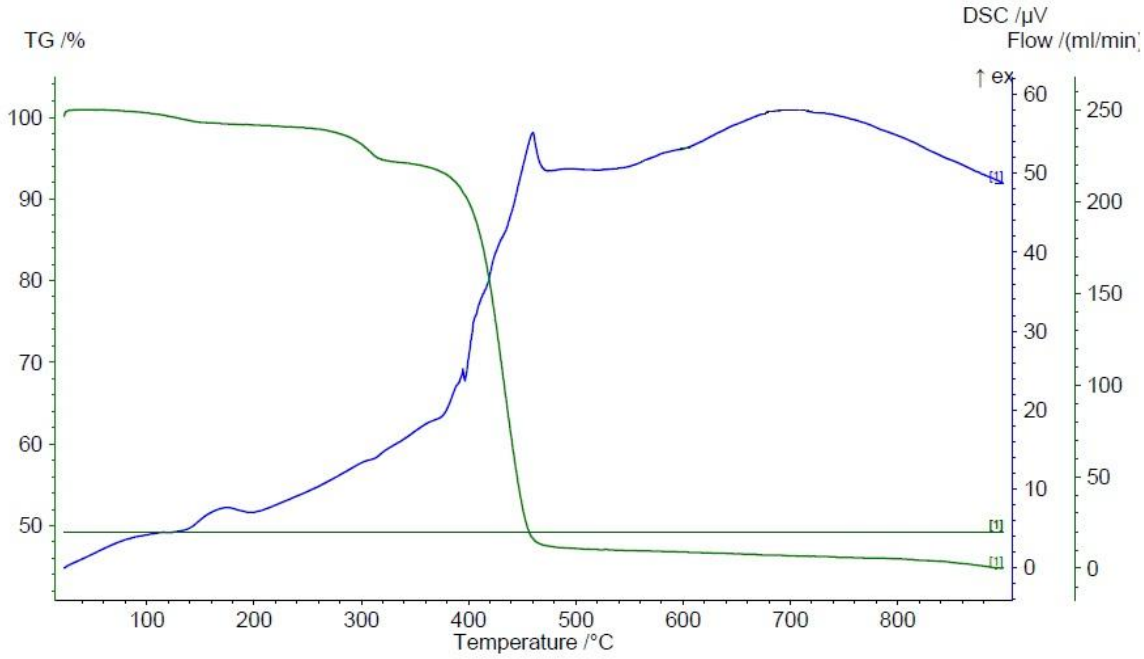


**Fig. 2** TG and DSC curves of PVP/zinc acetate precursor

Fig. 3 shows the FESEM micrographs and EDS spectrum of PVP/zinc acetate fibers obtained by electrospinning. The as-spun PVP/zinc acetate fiber Fig. 3(a) give a smooth surface while Fig. 3(b), 3(c) reveals that the surfaces of 500 °C annealed ZnO fiber consist of nanocrystallines which are connected to form a high surface area fiber, the crystallites are less than 100 nm in size. After annealed at 500 °C for 4 hours, the fibers remained continuous but the diameter becomes thinner, due to the decomposition of organic phase. Fig. 3(d) shows EDS Spectrum of a fiber annealed at 500 °C for 4 hours, the results clearly indicate that the presence of Zn in the fiber. The Si wafers were coated with $SiO_2$, which explains the reason of large percentage of Si and O being detected.

Fig. 4 shows the X-ray diffractograms for as-spun and calcined fibers, it is found that the as-spun fibers exhibited no apparent diffraction peaks, suggesting that the fibers were still in amorphous phase. On the other hand, the results indicate that electrospun fibers annealed at 500 °C for 4 hours were successfully converted to ZnO phase.

Fig. 5 shows the dynamic resistance response of the ZnO nanocrystalline fibers gas sensors as a function of time exposed to a range of concentration of $H_2$ testing gas. In this $H_2$ gas sensing test, time interval for every

$H_2$ flow and air purging was set to 300 s. The volume of gas chamber used for gas sensing test was 12 $cm^3$. Test results show that the sensor has good response to $H_2$ at room temperature. Sensitivity of the ZnO nanocrystalline fibers towards 2000 ppm of $H_2$ gas at room temperature is 4.92%. Lowest detection limit is 400 ppm $H_2$. It is observed that the gas sensor shows typical p-type sensing response to $H_2$, which the sensor resistance increased upon exposed to reducing gas.

The sensitivity (S) of the ZnO sensor towards $H_2$ gas was calculated using the following equation:

$$S = (R_g - R_0)/R_0 \times 100 \quad (1)$$

where, $R_0$ and $R_g$ are the sensor resistance in the absence and presence of $H_2$ gas.

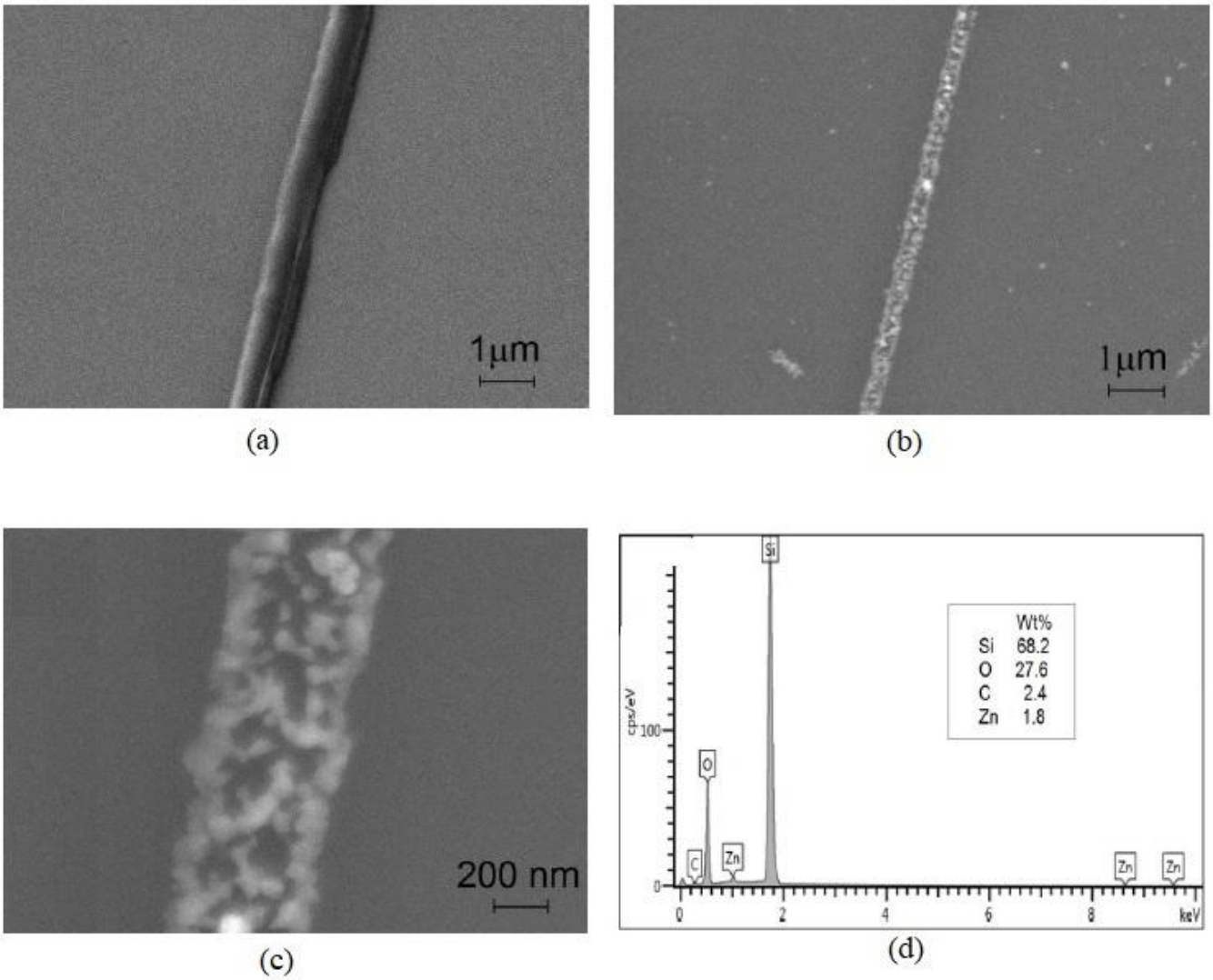


**Fig. 3** FESEM morphology (a) as-spun fiber, (b, c) annealed fiber at different magnification and (d) EDS spectrum of annealed fiber

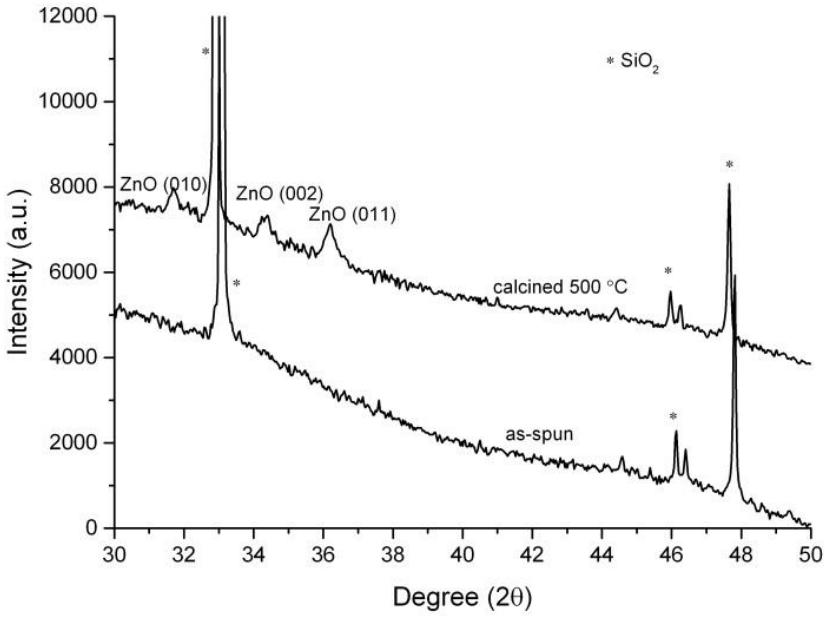


**Fig. 4** X-ray diffractograms for as-spun and calcined fibers

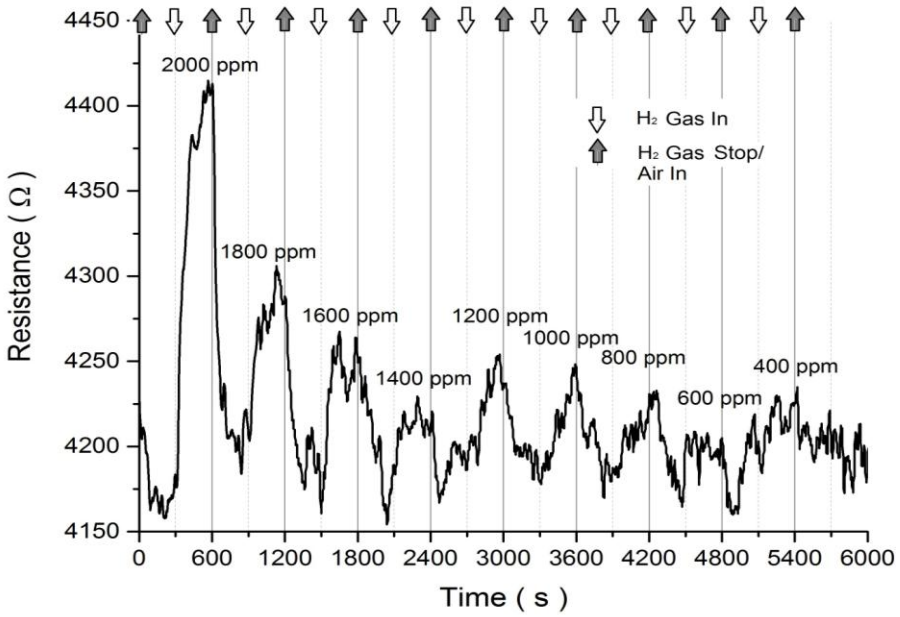


**Fig. 5** Dynamic resistance response of ZnO nanocrystalline fibers towards different concentration of $H_2$ at room temperature

## 4. SUMMARY

A room temperature hydrogen gas sensor was fabricated using ZnO nanocrystalline fibers. The fibers were prepared by electrospinning a precursor mixture of polyvinylpyrrolidone (PVP) and zinc acetate, followed by annealing at 500 °C for 4 hours in air. Annealed ZnO fiber consist of nanocrystallines which are connected to form a high surface area fiber, the crystallites are less than 100 nm in size. This work successfully demonstrated the sensing capability of ZnO nanocrystalline fibers toward $H_2$ gas at room temperature. Sensitivity of the ZnO nanocrystalline fibers towards 2000 ppm of $H_2$ gas at room temperature is 4.92% and the lowest detection limit is 400 ppm $H_2$.

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