

# A ZnO Nanorod Based 64° YX LiNbO<sub>3</sub> Surface Acoustic Wave CO Sensor

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**Abstract**— Zinc oxide (ZnO) nanorod based surface acoustic wave (SAW) gas sensor has been developed. ZnO nanorods were deposited onto a layered ZnO/64° YX LiNbO<sub>3</sub> substrate using a liquid solution method. Micro-characterization results reveal that the diameter and area density of ZnO nanorods are around 100 nm and 107 cm<sup>-2</sup>, respectively. The sensor was exposed to different concentrations of CO in synthetic air. The sensor response at operating temperatures between 200°C and 300°C was examined. The study showed that the sensor responded with highest frequency shift at 265°C. At this temperature, stable base-line and fast response and recovery were observed. The developed sensor is promising for industrial applications.

## I. INTRODUCTION

New gas sensing devices are required to meet increasingly stringent legal restrictions and industrial health and safety requirements, as well as for environmental monitoring, automotive applications and for manufacturing process control. To meet these demands, the sensitivity, selectivity and stability of conventional devices need to be drastically improved [1]. Recent advances in the development of nanostructured catalysts such as metal oxide nanoparticles, nanowires, nanorods and nanobelts [2-5] provide the opportunity to greatly increase the response of these materials, as sensor performance is directly related to granularity, porosity and ratio of surface area to volume in the sensing element. It has been established that the sensitivity of semiconductor metal oxide gas sensors increases with decreasing grain size [6], as the entire thickness of the sensitive layer can be affected by the redox reactions of the gas species. Thus, low dimensional nanostructured materials, which have an increased surface to volume ratio when compared to conventional polycrystalline structures, facilitate rapid diffusion of gases into and out of the materials' nano- and microporosities, which in turn increases the reaction rate, resulting in faster sensor response and recovery time. Semiconductor metal oxide thin films also offer low cost, consistent performance and easy fabrication [7]. In particular, zinc oxide films have been

investigated as sensors for H<sub>2</sub> [8], NO<sub>2</sub> [9], NH<sub>3</sub> [10], CH<sub>4</sub> [11], O<sub>2</sub> [12], CO [9] and ethanol [13]. The gas sensing capability is due to changes in the film conductivity in the presence of oxidizing or reducing gases.

Zinc oxide is one of the most promising electronic and photonic materials and has already been used in piezoelectric transducers, gas sensors, optical waveguides, transparent conductive films, varistors, solar cell windows and bulk acoustic wave devices [14-16]. As the ordered ZnO nanostructure has been envisioned to enhance performance of the above mentioned applications, the interest in synthesis well-aligned ZnO nanorods, nanowires and nanobelts on substrate keeps growing. Low dimensional ZnO nanorod based thin film gas sensors have been studied by a number of researchers [17-20] and reported that enhance performance has been achieved compared to coarse micrograined ZnO sensors.

In this paper we first deposited ZnO seed layer on a 64° YX LiNbO<sub>3</sub> SAW substrate using radio frequency (RF) sputtering. Then hydrothermal growth of high quality, densely packed and perpendicularly oriented single crystalline ZnO nanorods with average diameters of about 90 nm has been achieved. In SAW device, change in electrical conductivity perturbs the electro-acoustic properties of the propagating acoustic wave, resulting in a change in the velocity of the acoustic wave propagation. Deviations in velocity are monitored by measuring the changes in frequency. This change in frequency is directly proportional to the gas concentration in the environment. The developed nanorod based sensor then investigated towards CO gas. Finally, the dynamic responses of the sensor to different CO concentrations between 200°C and 300°C are presented.

## II. EXPERIMENTAL

The sensor consisted of two-port resonators with 38 electrode pairs in the input and output Inter Digital Transducers (IDT), 160 electrodes in each reflective grating, 700 μm aperture width and a periodicity of 40 μm. The center-to-center distance between the IDTs was 1920 μm.

The IDTs were formed by patterning an 80 nm layer of gold (Au) and a 20 nm titanium layer. The titanium layer is added to improve adhesion of the gold film.

To form a layered ZnO/64° YX LiNbO<sub>3</sub> substrate a 1.2 μm ZnO layer was deposited using RF sputtering. The ZnO layer was deposited from a 99.99% pure ZnO target with RF power of 120 W. The sputtering gas was 40% O<sub>2</sub> in Ar with a pressure of 10<sup>-2</sup> torr, a substrate temperature of 260°C and a deposition time of 60 minutes. This transparent ZnO layer acts as a seeding layer for the subsequent growth of the ZnO nanorods. Scanning electron microscope (SEM) images for sputtered ZnO growth on bare LiNbO<sub>3</sub> (left) and gold (right) are shown in Fig. 1.

To grow ZnO nanorod on the layered substrate, an aqueous solution of zinc nitrate hexa-hydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.0125M) and NaOH (0.5M) with a mole ratio of 1: 40 was used as the standard precursor solution. The growth temperature and duration were 70°C and 60 min, respectively. The procedure was similar to that described in the literature [21]. After growth, the sample was rinsed by deionized water. The SEM images (Figs. 2, 3 and 4) indicate that the ZnO nanorods density and morphology are different on the gold and LiNbO<sub>3</sub> surfaces. The nanorods are densely packed and vertically grown on top of gold IDTs (Fig. 3). On LiNbO<sub>3</sub>, the growth direction of nanorods has an angle with the surface (Fig. 4). The diameter and area density of ZnO nanorods are around 100 nm and 107 cm<sup>-2</sup>, respectively. The SEM images reveal that the surface of the nanorod thin film is highly porous which is essential for gas sensing.

The mechanism for nanorod growth is similar for almost all solution methods where a buffer layer of ZnO is usually pre-deposited on the substrate to promote nucleation and subsequent ordered nanorod growth. It has been reported that in hydrothermal synthesis the texture of the seed surface has great influence on the morphology and the alignment ordering of the ZnO nanorod arrays. In addition, the preparing conditions such as precursor concentration, growth temperature and deposition times also have an influence on the morphology of ZnO nanorods [22-23].

The gas sensor consist of two important physical components: the ZnO nanorods sensitive layer, which interacts with the gas media by changing conductivity, and the SAW transducer which changes its operating frequency in response to this conductivity change. Using the layered SAW device as a positive feedback element in a closed loop circuit with an amplifier, an oscillator was formed. A Fluke high-resolution counter (PM66860B) was used to measure the operational frequency of the sensor and found to be approximately 106.9 MHz in dry synthetic air at 265°C.

The sensor was mounted inside an enclosed environmental cell. Heating for the device was provided by a micro heater fabricated on a sapphire substrate with a patterned platinum resistive element. The heater was placed beneath the SAW sensor and controlled by a regulated DC power supply. A computerized mass flow controller (MFC) system was used to vary the concentration of CO in synthetic

air. The gas mixture was delivered at a constant flow rate of 0.2 liters per minute. Gas exposure time was fixed for each pulse of CO gas and the cell was purged with synthetic air between each pulse to allow the surface of the sensor to recover to atmospheric conditions. The sensor was exposed to a CO gas pulse sequence of 50, 100, 150 and 50 ppm concentrations in synthetic air at operating temperatures between 200 and 300°C.

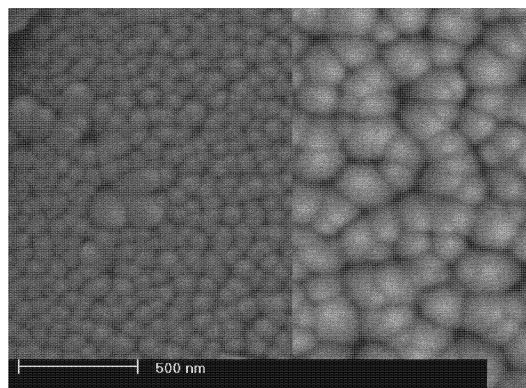


Figure 1. SEM image of sputtered ZnO seed layer growth on bare LiNbO<sub>3</sub> (left) and gold IDTs (right).

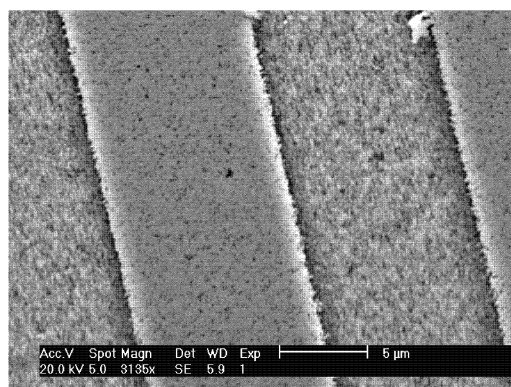


Figure 2. SEM image of ZnO nanorods on ZnO/64° YX LiNbO<sub>3</sub> substrate.

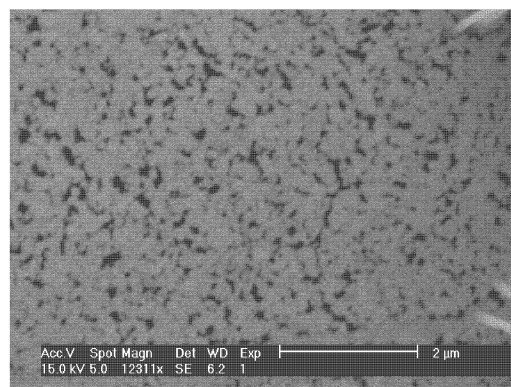


Figure 3. SEM image of ZnO nanorods growth on gold (Au) IDT's.

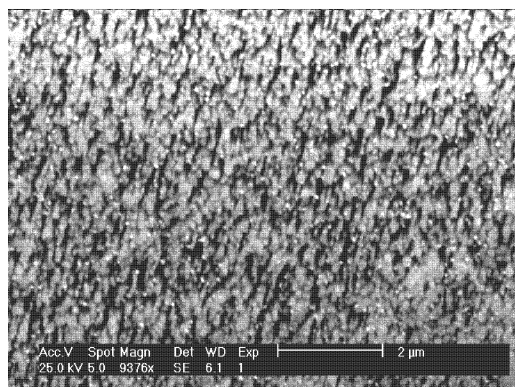


Figure 4. SEM image of ZnO nanorods growth on LiNbO<sub>3</sub>.

### III. RESULTS

The sensor requires an elevated operating temperature to enhance redox reactions so as to achieve the optimum sensitivity. The optimal operating temperature of the ZnO nanorod based sensor for CO sensing was found to be 265°C. Dynamic response of the ZnO nanorod based sensor towards different concentrations of CO at 265°C is shown in Fig. 5. The sensor response is defined as the variation in operating frequency of oscillation due to the interaction with the target gas. The measured response was 185 kHz towards 150 ppm of CO at 265°C with response and recovery of 20 and 32 sec, respectively. The response magnitude variation for the sensor to different CO concentrations is shown in Fig. 6. Frequency shift increases non-linearly with the increase of CO concentration. Frequency shift versus operating temperature for 150 ppm CO is shown in Fig. 7. ZnO nanorod based sensor operates at a lower optimum temperature with higher sensitivity than the other polycrystalline forms of ZnO based sensors for CO gas sensing.

The sensing mechanism is based on the reactions which occur at the sensor surface between the surface of nanorods and the CO molecules to be detected. It is well known that in an air environment, oxygen molecules adsorb onto the surface of the ZnO layer to form O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, O<sup>2-</sup> ions depending on temperature by extracting electrons from the conduction band [24-25]. The positively charged surface state and negatively charged adsorbed oxygen ions form a depletion region at the surface. Reducing gas such as CO gets oxidized to CO<sub>2</sub> consuming chemisorbed oxygen from the sensor surface by releasing electrons. This mechanism results in a reduction of surface depletion region to increase the film conductivity which corresponds to the gas concentration.

Reproducibility was observed as indicated when a second pulse of 50 ppm CO was introduced into the sensor chamber. It was found that the ZnO nanorod based sensor produce repeatable responses of the same magnitude with a stable baseline.

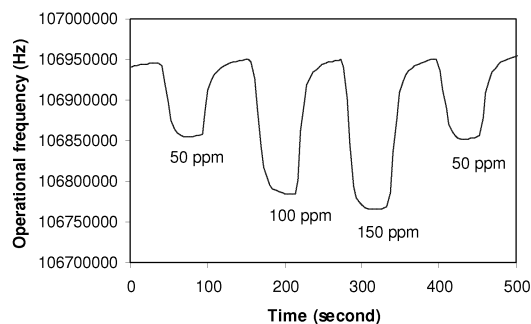


Figure 5. Dynamic response of the sensor to different CO gas concentrations in synthetic air at 265°C.

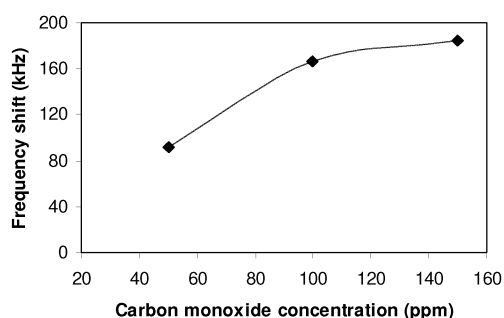


Figure 6. Frequency shift versus CO concentration (ppm).

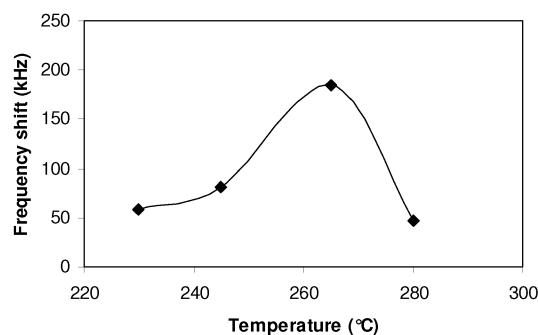


Figure 7. Frequency shift versus operating temperature for 150 ppm CO concentrations in synthetic air.

### IV. CONCLUSION

SAW gas sensor has been fabricated based on ZnO nanorod synthesized by simple hydrothermal process. The sensor has been investigated for its response to CO gas at different operating temperatures between 200 and 300°C. The sensor shows a repeatable and large response towards CO. Study shows that the optimum operating temperatures for the sensor are in the range of 260-270°C. The results demonstrate that the developed sensors are promising for industrial applications.

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