Research Article

A Surface Acoustic Wave Ethanol Sensor with Zinc Oxide Nanorods

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Surface acoustic wave (SAW) sensors are a class of piezoelectric MEMS sensors which can achieve high sensitivity and excellent robustness. A surface acoustic wave ethanol sensor using ZnO nanorods has been developed and tested. Vertically oriented ZnO nanorods were produced on a ZnO/128° rotated Y-cut LiNbO3 layered SAW device using a solution growth method with zinc nitrate, hexamethylenetetramine, and polyethyleneimine. The nanorods have average diameter of 45 nm and height of 1 μm. The SAW device has a wavelength of 60 μm and a center frequency of 66 MHz at room temperature. In testing at an operating temperature of 270°C with an ethanol concentration of 2300 ppm, the sensor exhibited a 24 KHz frequency shift. This represents a significant improvement in comparison to an otherwise identical sensor using a ZnO thin film without nanorods, which had a frequency shift of 9 KHz.

1. Introduction

Sensing of ethanol vapour has important applications in industry and society. At high temperatures (200°C to 300°C) zinc oxide absorbs ethanol vapour, causing a significant change in conductivity [1, 2] and also leading to a change in mass. This change in properties can be used to create an ethanol sensor.

Surface acoustic wave (SAW) sensors are a class of piezoelectric MEMS sensors which can achieve high sensitivity and excellent robustness. Since their discovery by Rayleigh in 1885 [3] surface acoustic waves have been extensively researched. The energy of a surface acoustic wave is concentrated within several wavelengths of the surface [4, 5]. For this reason, the propagation characteristics of surface acoustic waves are highly sensitive to any change in the properties of the surface on which they travel.

Due to the sensitivity of SAW devices to small changes in mass loading and surface conductivity, SAW devices have been extensively studied as gas sensors [6–8]. A typical SAW gas sensor uses an interdigital transducer (IDT) to generate a surface acoustic wave in a piezoelectric substrate. The surface acoustic wave propagates along a delay line coated in some material which absorbs the target gas. A second IDT at the end of the delay line is then used to transduce the SAW to an electrical signal. Absorption of gas onto the sensing layer causes a change in the propagation velocity of the surface acoustic wave, resulting in a shift in the resonant frequency of the device.

The majority of existing SAW gas sensors have used thin film sensing layers, with limited surface area. The application of nanostructured sensing layers, such as ZnO nanorods can potentially lead to improved sensing performance due to increased surface area. Promising results for SAW sensors using ZnO nanorods for hydrogen gas sensing [9, 10] and UV light detection [11] have been reported, although there have been few direct comparisons between the performance of these sensors and the performance of sensors using the same materials in thin film form.

2. Design and Fabrication

2.1. Sensor Design. The ZnO nanorod ethanol sensor was fabricated on a 128° rotated Y-cut LiNbO3 substrate. LiNbO3 offers excellent surface acoustic wave performance due to
the high-electromechanical-coupling coefficient \( k^2 = 4.5\% \) and low attenuation at high temperature [12].

The overall layout of the sensor is shown in Figure 1. Two interdigital transducers (IDTs), each consisting of 50 electrode pairs, are separated by a 12 mm delay line. The width of each IDT electrode and the spacing between the edges of adjacent IDT electrodes are 15 \( \mu \)m. The length of the IDT electrodes is 3 mm. The IDTs are oriented on the wafer so that SAW propagation is along the \( x \)-direction of the crystal. As shown in Figure 1, the substrate is cut at an angle to the SAW propagation direction to minimize reflections from the substrate edge on the side of the IDT away from the delay line [13].

The 15 \( \mu \)m electrode width and spacing result in the fundamental mode having a wavelength of 60 \( \mu \)m. The measured centre frequency of the devices at room temperature was 66 MHz. By the equation \( v = f \lambda \), this implies a propagation velocity of 3960 m s\(^{-1}\).

2.2. Fabrication Process. The metal electrodes and contacts were formed on the LiNbO\(_3\) wafer using a lift-off technique. The process used is illustrated in Figure 2.

AZ nLOF 2070 photoresist was spin-coated on the wafer and patterned (a). A 20 nm chromium layer followed by a 100 nm gold layer was then thermally evaporated (b) and the photoresist removed (lift-off process) to form the IDTs and contacts (c). A section of a fabricated IDT is shown in Figure 3.

The ZnO thin film and nanorods were produced only in the delay line of the device. The fabrication process used to deposit the ZnO thin film and grow the ZnO nanorods is summarized in Figure 4.

A photoresist layer was spin-coated and patterned with a window covering the delay line of the sensor (d). A 100 nm ZnO layer was then deposited by sputtering from a ZnO ceramic target (e). In order to obtain a good quality film, the DC sputtering was carried out at a pressure of 2.7 Pa, in an atmosphere with 80% argon and 20% oxygen. The current used was 0.25 A DC. The photoresist was then removed in acetone, leaving the ZnO thin film, which serves as a seed layer for nanorod growth (f). Finally, the ZnO nanorods were produced by a solution growth technique [14] (g). The devices were suspended ZnO-side-down in a sealed bottle containing a solution of zinc nitrate, hexamethylenetetramine, and polyethyleneimine in deionized water. The sealed bottle was then incubated in a laboratory oven at 95 °C for 4 hours, after which the substrates were removed from the solution, rinsed with 95 °C DI water, and allowed to air-dry at room temperature. The growth parameters were selected to give a uniform layer of predominantly vertical nanorods which adhered well to the substrate. Nanorods produced by this method are shown in Figure 5. The nanorods formed are vertical and well defined, with average diameter 45 nm and height 1 \( \mu \)m.

2.3. Measuring System. The ethanol sensors produced were characterized using general purpose laboratory equipment controlled from the computer, as illustrated in Figure 6. An Agilent 33250A function generator was programmed to apply an excitation voltage to one IDT of the sensor. The magnitude and phase of this waveform, and of the waveform from the second IDT, were monitored using an Agilent 6102A DSO.

The propagation velocity of surface acoustic waves in LiNbO\(_3\) is temperature dependent. The absorption of ethanol onto ZnO nanorods is also temperature sensitive [15]. Therefore, in order to detect low concentrations of ethanol vapour, the sensor temperature must be tightly controlled. A platinum thin film resistance thermometer on the substrate was used to monitor the operating temperature of the device during measurement. For characterization, the sensor was heated using a laboratory hot plate. Testing of sensitivity to
ethanol was performed with the sensor in a sealed chamber, in which the heated sensor could be alternately exposed to a known concentration of ethanol and flushed with air to allow adsorbed ethanol to desorb from the ZnO layer.

3. Results

The response of the SAW ethanol sensor using ZnO nanorods to a known concentration of ethanol was measured. In order to demonstrate that the ZnO nanorods provided a benefit for ethanol sensing, the shift in the frequency response of the sensor with nanorods was compared with that of an otherwise identical device with the sputtered ZnO thin film, but lacking the ZnO nanorod layer. In the oscillator configuration commonly used for SAW gas sensors, the oscillation frequency is determined by the frequency at which the phase shift around the loop is some integer multiple of $2\pi$ [16]. Therefore, the results presented are given in terms of the phase shift between the wave input to one IDT of the sensor and the wave received at the second IDT, after propagating through the nanorod layer.

The effect of 2300 ppm ethanol on the phase shift of a sample with nanorods at 270°C is presented as Figure 7. Results under the same conditions for a sample without nanorods are shown in Figure 8. It was noted that the shape of the phase response for the sensor with nanorods differed from that of the sensor with ZnO thin film. This was attributed to increased mechanical damping caused by the nanorod layer.

The maximum frequency offset between the phase response plot obtained with air in the chamber and the phase response obtained with 2300 ppm ethanol in air in the chamber was 24 KHz for the sensor with ZnO nanorods. In comparison, the maximum frequency offset under these conditions with ZnO thin film only was 9 kHz. The 24 kHz frequency shift obtained for the sample with ZnO nanorods subjected to 2300 ppm ethanol, expressed as a fraction of the 64.3 MHz frequency where this shift occurred, is 370 ppm. In comparison, the fractional frequency shift for the sample without ZnO nanorods was 140 ppm.

The sensor’s response time is estimated by measuring the phase shift between the input and output signal at a particular frequency (64.37 MHz) as shown in Figure 9. A 2.5 mL of ethanol was vaporized at approximately 340 s. The sensor took approximately 200 s to reach its maximum phase shift at 640 s. The phase shift remains at approximately $-15.1°$ for another 200 s before it starts to recover. From
Figure 9, the sensor seems to take a longer time to recover. After waiting for approximately 240 s, the sensor has yet to fully recover to its initial phase shift. It is believed that at higher temperature, the response and recovery time could be shortened but this requires further investigation. Nevertheless, we have demonstrated that the use of nanorods increased the sensitivity of the sensor.

4. Conclusions

A novel surface acoustic wave ethanol sensor using ZnO nanorods was developed and tested. The change in frequency response that occurred when the sensor was exposed to ethanol was measured and compared to that of a sensor using a ZnO thin film only. The SAW ethanol sensor with ZnO nanorods demonstrated a frequency shift of 24 kHz in response to 2300 ppm ethanol at 270° C, a significant improvement over the 9 kHz shift of the sensor without nanorods. The application of a nanorod sensing layer is a promising technique to improve the sensitivity of surface acoustic wave gas sensors, albeit the long response and recovery time.

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