Layered SAW hydrogen sensor with modified tungsten trioxide selective layer

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Abstract
Layered surface acoustic wave (SAW) devices are investigated for sensing hydrogen (H2) concentrations less than 1% in air. Platinum (Pt) and gold (Au) catalyst activated tungsten trioxide (WO3) selective layers are investigated. The SAW sensors consist of two thin film metal interdigital transducers (IDTs) on a 36° Y-cut, X-propagating LiTaO3 substrate. A ZnO guiding layer is used to confine the acoustic energy at the active surface of the device for increased sensitivity. In this paper, the fabrication of an Au–WO3 and a Pt–WO3 based layered SAW device are described. The sensor response have been analysed in terms of frequency shift as a function of different hydrogen concentrations and operating temperatures. The responses of the catalyst activated WO3 sensors show much higher sensitivity when compared against a layered SAW sensor employing only a bare WO3 selective layer. Frequency shifts of 705 and 118 kHz towards 1% H2 in air were observed for the Au–WO3 and Pt–WO3 sensors, respectively. Characterization by scanning electron microscope (SEM) of the Au catalyst activated tungsten trioxide sensor is also presented.

Keywords: Layered; SAW; Hydrogen Catalyst; Tungsten trioxide

1. Introduction
The utilization of hydrogen as a source of clean abundant energy has been a widely pursued topic for many years. It has been heavily used in space programs and industry, for several decades. It has been proven to be useful in many applications, such as: petroleum transformation, semiconductor manufacturing, cryogenics, fuel cells and rocket engines just to name a few. The hazards associated with the storage and usage of hydrogen has always posed a tremendous problem. Hydrogen’s small molecular size enables it to penetrate into metals, causing corrosion and deteriorating properties such as strength and durability.

The operation of most gas sensors is based on the reversible changes in the conductivity, particularly for technologies based on metal oxide semiconductor (MOS) films. Tungsten trioxide is an n-type semiconductor and has been reported extensively as an electrochromic material. The use of WO3 as a selective layer for electrochromic [1], optical [2], chemiresistive [3] and SAW [4–7] gas sensor has been reported in literature. Tungsten trioxide is also well known to interact with H2S, O3, NOx, NH3 and H2 gases [8–10].

Recently, the authors reported a layered SAW gas sensor employing a WO3 selective layer for hydrogen gas concentration less than 1% in air [11]. For work reported here, a similar ZnO/YX LiTaO3 layered SAW structure is presented, however the effects of modifying the WO3 selective layer surface with thin sputtered platinum (Pt) and gold (Au) metals are investigated at different operating temperatures.

It is well known that improvements in sensitivity and selectivity of semiconductor based gas sensors can be achieved by the addition of metal catalytic activators. As early as 1967, Shaver [12] illustrated that a Pt activated WO3 based gas sensor. DOI: 10.1016/j.snb.2004.11.048
The catalyst activators can significantly strengthen the reactions between the target gas and MOS surface, as well as reducing the response and recovery times [13]. Tao and Tsai reported 1–2 nm of Pt, Au or combined Au–Pt thin film over WO3 selective layer for H2S sensing applications. The Pt film showed highest sensitivity towards 1 ppm of H2S and the Au–Pt film towards 1 ppm H2 [14]. It was also cautioned, that if the amount of catalyst is too much, the catalyst could be oxidized at high temperatures, deteriorating the sensor’s response characteristics.

The reduction of pure WO3 by hydrogen begins above 400 °C. However, it is understood that this reaction proceeds readily even at room temperature in the presence of noble metal catalyst activators, such as Pt or Pd [15]. Hydrogen gas dissociates on the catalyst activator into hydrogen atoms. The change in conductivity of the WO3 selective layer causes a change in the sheet conductivity of the Au–WO3 and Au–Pt thin film, via DC sputtering at room temperature. Fig. 1 shows a cross-section of the layered SAW structure. The thickness of the Pt and Au layers are estimated to be approximately 4 and 6 nm, respectively. The films deposited are assumed to be a non-continuous film at these thicknesses. In both cases, it was observed that the structure changed in color after the catalyst deposition. A greenish and a blackish color were observed for the Au and Pt layers, respectively.

Previous work dealing with the characterization of ZnO on 36° FX LiTaO3 can be found in [11,19]. The ZnO growth is orthogonal to the surface of the 36° FX LiTaO3 substrate. Fig. 2 is a SEM micrograph illustrating the ZnO grain boundaries, which are only partially visible through the bare WO3 layer. The WO3 thin film does not appear to be oxidized at high temperatures, deteriorating the sensor’s response characteristics.

The effect of aggregation of Au on WO3 films is illustrated by SEM image in Fig. 3. The gold particles on the WO3 surface increase in size and decrease in number density over time, via accelerated aging [20]. The aggregation into larger particles found to occur could pose significant changes in the sensitivity of a sensor. SEM characterization of the sensor was taken after the aggregation process.
the experimental procedure was completed. The sensors were elevated to temperatures up to 290 °C for a prolonged time, which is outlined in Section 3. Attempts were made to image the Pt–WO3 sensor; however difficulty was experienced in gaining a focused image due to charging of the sample.

3. Experimental

Hydrogen adsorption and desorption on the WO3 surface causes velocity changes in the acoustic waves. The SAW sensor being tested was used as the frequency control element in an oscillator circuit. A computer was used to data-log a frequency counter (Fluke PM6680B) that monitored the oscillation frequency. The SAW sensor was mounted on a micro-heater and enclosed in a cell of approximately 30 ml. The micro-heater was controlled by a regulated DC power supply, providing the different operating temperatures. A computerized gas calibration system, with mass flow controllers, was used to mix and deliver five different concentrations of H2 at a constant flow rate of 0.2 l/min. Synthetic air was used as both the reference gas and the diluting gas. The sensor was exposed to a pulse sequence of 0.06, 0.125, 0.25, 0.50, 1.0 and 0.06% of H2 in air at each operating temperature. Each pulse in the sequence used an exposure time of 180 or 240 s and a recovery time of 360 or 480 s, respectively.

Both the Au-WO3 and Pt-WO3 SAW sensors were tested separately. Care was taken to ensure the sensors were tested under the same conditions using the same protocol. They were cycled over a period of two weeks. Each sensor was tested between the range of 30 and 290 °C in increments of approximately 27 °C. At each operating temperature, the sensor was held for a period of 90 min to stabilize, and then tested towards two discrete pulse sequences of hydrogen. A 2 h period in between each pulse sequence was used.

4. Results and discussion

The deposition of the Pt and Au thin catalyst activators on the surface of the WO3 layer greatly improves the performance of the sensor. The Pt-WO3 and Au-WO3 sensors at room temperature were observed to have an operating frequency of approximately 168.66 and 166.58 MHz, respectively. Both sensors exhibited different sensitivities at different operating temperatures. It was found that the Pt-WO3 sensor generally had a quicker response and recovery time than the Au-WO3 sensor, however the difference was found to be marginal. Fig. 4 shows the response of the Pt-WO3 sensor towards H2 pulse sequence (0.06, 0.125, 0.25, 0.50, 1.0 and 0.06%) in air at operating temperatures of 270 °C (above) and 100 °C (below).
sensor at operating temperatures of 100 and 270 °C. The response of the Au–WO₃ sensor at operating temperatures of 245 and 270 °C is shown in Fig. 5.

In [11], the bare WO₃ layer was observed to have 11 and 25.8 kHz frequency shifts for 0.5 and 1% H₂, respectively. The response of the catalyst activated sensors, Pt–WO₃ and Au–WO₃, produced a frequency shift approximately 5 and 50 times larger than the bare WO₃ layer for a hydrogen concentration of 0.5%, respectively. Fig. 6 shows the frequency shift observed for each tested H₂ concentration at the different operating temperatures. It can be seen that both the Pt–WO₃ and Au–WO₃ sensors produced the largest frequency shift at an operating temperature of approximately 270 °C.

The Au–WO₃ sensor was observed to have a single point of maximum sensitivity, at approximately 270 °C, as opposed to the two distinct points for the Pt–WO₃ sensor at 100 and 270 °C. The lower operating temperature of 100 °C demonstrates a higher sensitivity towards hydrogen concentrations below 0.5% than measured at 270 °C for the Pt–WO₃ sensor. This could be a considerable advantage of the Pt–WO₃ sensor, as a lower power consumption device. The Pt–WO₃ sensor may have shown even higher sensitivity at operating temperatures above the 270 °C. However, these temperatures are beyond the test system limitations. Overall, the Au–WO₃ sensor was observed to show the highest sensitivity. These trends are clearly visible in Fig. 6. Table 1 lists the frequency shift observed for each sensor at the operating temperature of interest.

The stability of both the Pt–WO₃ and Au–WO₃ sensors were found to be superior to that of the bare WO₃ tested previously. This was attributed to improvements of the testing setup made in between experiments. Due to the increase in response magnitude, the frequency drift in the oscillators output signal is much less significant. Unfortunately, over the 2-week testing period of each sensor, changes in response magnitude of the Pt and Au activated WO₃ sensors were encountered. Long-term stability problems with Pt and Au doped WO₃ films due to ageing effects of the catalysts are well known [21]. It has also been reported that possible changes in the morphology of the metal particles on the sensing film at elevated temperatures could cause drift in gas sensitivity [20]. Continual testing and further work would be required to stabilize the metal particles on the MOS surface to resolve these issues.

### Table 1 Calculated sensitivities for the tested H₂ concentrations at optimal operating temperatures

<table>
<thead>
<tr>
<th>Selective layer</th>
<th>Operating temperature (°C)</th>
<th>Center frequency (MHz)</th>
<th>Frequency shift (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.06%</td>
</tr>
<tr>
<td>WO₃</td>
<td>175</td>
<td>164.0</td>
<td></td>
</tr>
<tr>
<td>Pt–WO₃</td>
<td>270</td>
<td>166.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Pt–WO₃</td>
<td>100</td>
<td>166.6</td>
<td>6.6</td>
</tr>
<tr>
<td>Au–WO₃</td>
<td>270</td>
<td>165.3</td>
<td>187.0</td>
</tr>
<tr>
<td>Au–WO₃</td>
<td>245</td>
<td>165.7</td>
<td>55.4</td>
</tr>
</tbody>
</table>

* Results quoted from previous work [11].
5. Conclusions

Platinum and gold catalyst activated WO$_3$ layered SAW devices were fabricated and tested towards $H_2$ concentration below 1% in synthetic air. The sensors were based on ZrO$_{36}$/3% Y LiTaO$_3$. SAW delay lines operating at approximately 165-168 MHz. The response of the sensors with Pt and Au catalyst activator layers produced a frequency shift approximately 5 and 50 times larger than bare WO$_3$ layer for a hydrogen concentration of 0.5%, respectively. The sensors exhibited different response to hydrogen at different temperatures. It was observed that the Pt-WO$_3$ sensor showed maximum sensitivity at operating temperatures 100 and 270°C, while the Au-WO$_3$ sensor showed best performance at 245 and 270°C. The results presented show that high sensitivity can be achieved utilizing a layered SAW structure with SH-SAW for gas sensing applications.

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References


Biographies

S.J. Ippolito received the Bachelor of Engineering degree in computer systems engineering (with honours) from RMIT University, Melbourne, Australia, 2002. He is currently pursuing the PhD degree in sensor technology at RMIT University. His major research interest areas include the fabrication and application of layered surface acoustic wave chemical sensors based on thin film technology.

K. Kandasamy received his Bachelor of Engineering from the Bharathidasan University, Tamilnadu, India in June 2000. He completed his Master of Engineering degree in electronics with specialization in MEMS at RMIT University, Melbourne, Australia in December 2003. He is currently undertaking his PhD at RMIT University, with his major areas of research being microelectronics; SAW gas sensors and Schottky diode based high temperature gas sensing.

W. Wlodarski has worked in the areas of sensor technology and instrumentation for over 30 years. He has published four books and monographs, over 400 papers and holds 29 patents. He is a professor at RMIT University, Melbourne, Australia, and heads the Sensor Technology Laboratory at the School of Electrical and Computer Engineering.