**Proceedings of the 2003 IEEE International Frequency Control Symposium and PDA Exhibition Jointly with the 17th European Frequency and Time Forum**

# LAYERED SAW NITROGEN DIOXIDE SENSOR BASED ON A ZnO/ 36º YX $LiTaO_3$ STRUCTURE WITH $WO_3$ SELECTIVE LAYER

S. J. Ippolito[1,2], K. Kalantar-Zadeh[1,2], A. Trinchi[1,2], W. Wlodarski[1,2], M. Tobar[3]

[1]RMIT University, School of Electrical and Computer Systems Engineering, Melbourne, AUSTRALIA
[2]CRC for Micro-Technology, Hawthorn, VIC 3122, AUSTRALIA
[3]University of Western Australia, Department of Physics, AUSTRALIA

*Abstract* - **A novel layered Surface Acoustic Wave (SAW) device is investigated for gas sensing of low levels $NO_2$ concentrations in air. The results show much higher sensitivity when compared against other SAW devices operating at the same frequency. The sensing structure is based on a layered SAW devices fabricated on a 36° X-cut, Y-propagating $LiTaO_3$ substrate. A ZnO guiding layer is employed to increase sensor sensitivity, whilst a thin film of $WO_3$ provides the selectivity towards $NO_2$. In this paper, the fabrication of the ZnO/36° YX $LiTaO_3$ sensor is described and micro-characterization of the selective layer is presented. Furthermore, a gas sensing experiment reveals the sensitivity of the device.**

***Keywords*** **- Layered SAW, $NO_2$, Gas sensing, 36° YX $LiTaO_3$, ZnO**

## I. INTRODUCTION

Semiconductor metal oxide (SMO) films have been used extensively for toxic gas sensing. A sensor response using a metal oxide selective film is based upon sheet conductivity changes caused by interaction with gas molecules. Such changes in electrical conductivity have been noted since the earliest studies of semiconducting materials [1],[2]. Many reactions on the surface of metal oxides are possible which can be acceptable as the gas sensing mechanism. However, the most dominant reaction in semiconductor gas sensing is a reversible gas adsorption mechanism that occurs on the sensor's surface. The adsorbed gas atoms inject electrons into or extract electrons from the semiconducting material, depending on whether they are reducing or oxidizing respectively [3].

Nitrogen dioxide ($NO_2$), even at low ppm concentration levels, is hazardous for human health. Therefore, the development of sensors capable of measuring low concentrations of this gas is of significant importance. Tungsten trioxide ($WO_3$) films have been reported to show remarkable sensitive properties to $NO_2$ [4].

By the deposition of a SMO layer onto the active area of a SAW device, the device can be used for gas sensing applications. In a SAW device, the change in electrical conductivity perturbs the electro-acoustic properties of the underlying propagating acoustic wave. This results in the propagating acoustic wave changing its velocity. Deviations in velocity are monitored by measuring the changes in frequency or phase characteristics of the sensing device. Thus the frequency or phase characteristics can be correlated to the corresponding concentration of the targeted gas exposed to the device.

Layered SAW transducers have shown significant attention in recent years for sensing applications [5],[6]. An increase in the confinement of acoustic energy at the surface of the device is made possible by using layered structures. The deposition of a piezoelectric guiding layer, such as zinc oxide (ZnO) generally results in further increasing the sensitivity of the device. ZnO is a piezoelectric material with a large electromechanical coupling coefficient [7]. The deposition of a ZnO layer onto the 36° XY $LiTaO_3$ substrate forms a layered SAW structure. Shoji et al. [8],[9] showed that deposition of ZnO layer onto 36° YX $LiTaO_3$ substrates results in an increased electromechanical coupling coefficient ($K^2$) for the SAW device. Prior to the deposition, a shear horizontal (SH) particle displacement with minimal normal component is the dominant acoustic wave propagation mode. After the deposition of the ZnO layer, SH displacement still retains. As a result, the sensor can operate in both gas and liquid media. The overall effect is the device having an enhanced sensitivity to perturbations caused by gas molecule interactions with the selective layer when compared to non-layered SAW device counterparts.

In this paper, a layered SAW structure based on ZnO/ 36° YX $LiTaO_3$ substrate is presented for $NO_2$ gas sensing applications. The design, fabrication and characterization of the deposited thin film are investigated. Finally, the response of the sensor to different $NO_2$ gas concentration is illustrated.

## II. SENSOR FABRICATION

The sensor consisted of a two-port delay line with 64 input and output Inter Digital Transducer (IDT) finger pairs, 1.25mm aperture width and a periodicity of 24μm. The center-to-center distance between the IDTs was 85 wavelengths. The IDTs were formed by patterning a 2500Å aluminium layer and a 300Å layer of chromium. The aluminium layer was deposited upon the chromium to improved adhesion to the substrate.

Devices were fabricated with ZnO layer thickness of 1.2μm, deposited by an RF planar magnetron sputterer, using a

99.99% pure ZnO target. Sputtering gas was 40% $O_2$ in Ar and RF power was 120W, resulting in a deposition rate of ~1.2μm/hour.

The $WO_3$ selective layer was deposited by RF planar magnetron sputterer, using a 99.99% pure tungsten target. Using a mixture of 90% $O_2$ and 10% Ar, a deposition rate of approximately ~0.32μm per hour was achieved for 80W of the R.F. power. The sample was sputtered for duration of half an hour, resulting in a thickness of 0.16μm.

Both the ZnO and $WO_3$ where sputtered at a pressure of $1.0\times10^{-2}$ Torr using the same substrate conditions of 260°C and at a distance of 6.5cm from the target.

## III. Material Analysis

The surface morphology of the ZnO film deposited onto a 36° YX $LiTaO_2$ substrate was characterized by Scanning Electron Microscopy (SEM) and the crystallinity by X-Ray Diffraction (XRD) analysis in pervious work [10]. Fig. 1 (a) shows the XRD pattern is seen of a 1.2μm layer of ZnO. The XRD pattern of the same structure with the addition of a 0.16μm layer of $WO_3$ deposited on top of the ZnO is shown in Fig. 1 (b).

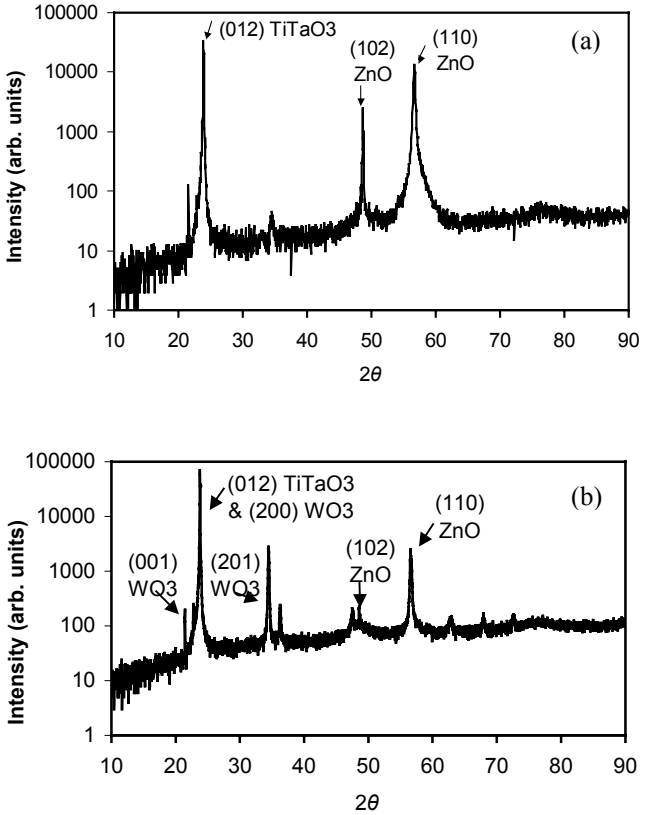


Fig 1. (a) XRD pattern of a 1.2μm layer of ZnO on $LiTaO_3$ substrate. (b) XRD XRD pattern of 750Å of $WO_3$ on a 1.2μm layer of ZnO on $LiTaO_3$ substrate.

From these results presented, a strong ZnO (110) peak indicates that the c-axis lies in the plane of the substrate. The presence of a smaller ZnO (102) peak is also seen, however, is dominated by the (110) peak [10]. XRD analysis of the sample with the $WO_3$ reveals the two peaks at angles of $2\theta$ equaling 34.5º and 36.5º, respectively. At the position of the $LiTaO_3$ (012) main peak, it can be seen that the intensity of the peak is substantially increased. Cantalini and et al. [11] where able to show the existence of peak at 2θ equals 24 degrees when $WO_3$ is RF sputtered, which would suggest that the $LiTaO_3$ and $WO_3$ peaks overlap at this position. They also showed that a (201) peak at $2\theta$ equals 34.5º correlates with $WO_3$ and that $Al_2O_3$ is represented by the peak at $2\theta$ equals 36.5º. Hence, the same peak observed in Fig. 1 (b), where $2\theta$ equals 36.5º, could be attributed to $Al_2O_3$ contamination during the $WO_3$ deposition.

## IV. Sensitivity Analysis

The theoretical change of the device's operational frequency, produced by the change in conductivity of the selective layer can be derived using perturbation theory, assuming weak coupling [6],

$$|\Delta f| = f\frac{K^2}{2}\frac{1}{1+\left(\frac{V_o(\varepsilon_s+\varepsilon_A)}{\sigma.d}\right)^2}, \qquad (1)$$

where $f$ is the operational frequency, $\Delta f$ is the relative frequency change due to the conductivity change of the surface and $K^2$ is the electromechanical coupling coefficient. The variables that are a function of the deposited films are: $V_o$, the acoustic wave velocity that propagates in the substrate; σ, the bulk conductivity of the layer; and $d$ defined as the layer thickness. The substrate and ambient atmospheric dialectic constants are $\varepsilon_s$ and $\varepsilon_A$, respectively.

The decrease of the $WO_3$ film's conductivity is attributed to interaction with the $NO_2$, which is an oxidizing gas. As $WO_3$ is regarded as having a non-stoichiometric structure, free electrons originating from oxygen vacancies contribute to the conductivity of the thin film, outlined in (2),

$$O_{O\,(bulk)} = V_o + 2e' + \tfrac{1}{2}O_{2\,(gas)}, \qquad (2)$$

where $V_o$ is the vacancies and the $O_{O\,(bulk)}$ is present in the $WO_3$ layer. Due to the extra electron generated $WO_3$ is categorized an n-type semiconductor. Upon the introduction of the $NO_2$, it reacts with the $WO_3$ layer, decreasing the film's conductivity.

## V. Gas Sensitivity Analysis

The response of the sensor to low $NO_2$ concentrations (less than 1 ppb) levels in a balance of dry air is presented (Fig. 2). The sensor was placed in a computerized gas calibration system, where different concentrations of $NO_2$ gas was delivered via mass flow controllers. The operational temperature, linearity, recovery and response time were all analyzed and related to the $NO_2$ concentrations.

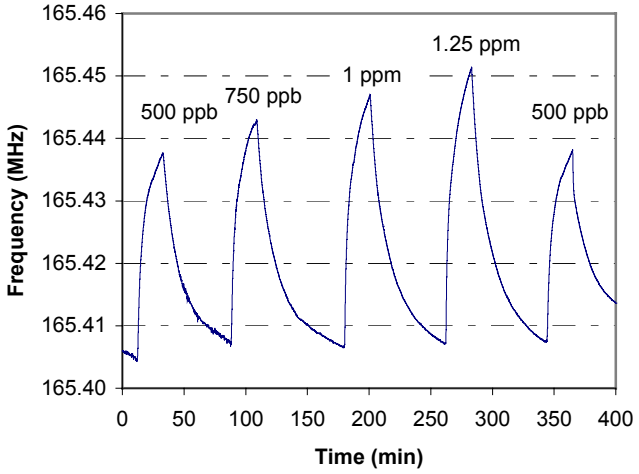


Fig. 2. Dynamic response of $WO_3$ based SAW sensor to different $NO_2$ concentrations at an operating temperature of 100°C and gas flow rate of 0.3 liters per minute.

The operational frequency of the device was approximately 165.406 MHz in air, at an operating temperature of around 100°C. At this operating temperature, preferred sensing characteristics (i.e. response repeatability to $NO_2$ concentrations) were observed. Additionally at 100°C, the maximum response was observed, yielding the highest frequency shift for a fixed concentration of $NO_2$, namely 1.25 ppm. It was found that linear increases in operational frequency were achieved by the introduction of $NO_2$, up to the saturation level of 1.5 ppm. Repeatability was also observed, when successive $NO_2$ pulses of 500 ppb were introduced to the sensor chamber. At this concentration a frequency shift of approximately 30 KHz was observed and is also presented in Fig. 2. The associated frequency shifts for 500ppb to 1.25ppm concentrations of $NO_2$ mixed with synthetic air are presented in Table 1.

TABLE I
FREQUENCY SHIFT VS $NO_2$ GAS CONCENTRATION

| Nitrogen dioxide concentration | Shift in center frequency |
|---|---|
| 1.25 ppm | 43.86 kHz |
| 1.00 ppm | 39.45 kHz |
| 750 ppb | 35.62 kHz |
| 500 ppb | 30.22 kHz |

Despite the large frequency shifts observed for such low concentrations, the sensor response times were long, and hence the gas exposure time was fixed at 20 minutes for each pulse of the analyte gas. The sensor returned to the same baseline frequency (165.406 MHz) following each $NO_2$ pulse, however the recovery time was approximately 58 minutes. It is believed that such long recovery times are due to the thickness of the $WO_3$ selective layer (0.16 μm). Tests are currently being conducted with thinner $WO_3$ layers in order to examine the effect of selective layer thickness against response and recovery times of the sensor. Furthermore, due to the limitations of the gas delivery equipment, responses to lower than 500 ppb concentrations of $NO_2$ were not able to be tested.

## VI. Conclusion

The sensor response based on ZnO/ 36° YX $LiTaO_3$ structure was investigated for different concentrations of $NO_2$ gas in air. The operational frequency of the device was approximately 165 MHz. Linear increases in operational frequency are achieved by the introduction of $NO_2$, up to the saturation level of 1.5 ppm $NO_2$. A concentration of 500 ppb shows an approximate 30 KHz response.

Further investigations are planned where the optimal thickness of the selective layer will be studied. Furthermore, the effect of increasing the center frequency of the transducer will be tested in a bid to increase the sensitivity of the layered SAW device.

## Acknowledgment

The authors would like to thank CRC for Micro-Technology, Australia, for financial support.

## References

[1] A. Many, Y. Goldstein, N.B. Grover, in: Semiconductor Surfaces, North Holland, Amsterdam, 1965.
[2] S. R. Morrisson, in: Chemical Physics of Surfaces, Plenum Press, New York, 1977.
[3] P. Kofstad, in: Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides, Wiley, New York, 1983.
[4] C. Cantalini, H.T Sun, M. Faccio, M. Pelino, S. Santucci, L. Lozzi, M. Passacantando, "$NO_2$

Sensitivity of $WO_3$ Thin Film Obtained by High Vacuum Thermal Evaporation," *Sensors and Actuators B*, vol. 31, pp. 81-87, 1996.

[5] K. Kalantar-Zadeh, A. Trinchi, W.Wlodarski, A. Holland, M. Z. Atashbar, "A Novel Love Mode Device with Nanocrystalline ZnO Film for Gas Sensing Applications," *Proc. of the 1st IEEE-NANO Conference*, pp. 556 –561, 2001.

[6] K. Kalantar-zadeh, A. Trinchi, W. Wlodarski, A. Holland, **"**A Novel Love-mode Device Based on a ZnO/ST-cut Quartz Crystal Structure for Sensing Applications," *Sensors and Actuators A: Physical*, vol. 100, pp. 135-143, 2002.

[7] J. Xu, Q. Pan, Y. Shun, Z. Tian, "Grain Size Control and Gas Sensing Properties of ZnO Gas Sensor," *Sensors and Actuators B*, vol. 66, pp. 277-279, 2000.

[8] K. Nakamura, T. Shoji and H.B. Kang, "Growth of ZnO Films on (012) $LiTaO_3$ by ECR-MBE and Determination of Their Polarity," *Proc. Int. Symp. App. Ferroelec.*, pp. 467-470, 2000.

[9] T. Shoji, K. Nakamura and D. Yamazaki, "Propagation Characteristics of the SH-SAW on (110) ZnO/ (012) $LiTaO_3$," *Proc. IEEE Ultrason. Symp.*, pp. 215-219, 2001.

[10] D. A. Powell, K. Kalantar-zadeh, S. Ippolito, W. Wlodarski, "A Layered SAW Device Based on ZnO/$LiTaO_3$ for Liquid Media Sensing Applications," *Proc. of IEEE Ultrasonics Symposium 2002, Munich, Germany,* pp. 493-496, 2002.

[11] C. Cantalini, W. Wlodarski, Y. Li, M. Passacantando, S. Santucci, E. Comini, G. Faglia and G. Sberveglieri, "Investigation on the $O_3$ Sensitivity Properties of $WO_3$ Thin Films Prepared by Sol–gel, Thermal Evaporation and r.f. Sputtering Techniques," *Sensors and Actuators B*, vol. 64, Issues 1-3, pp. 182-188, 2000.