Ozone Sensors based on Layered SAW Devices with: InO_x / SiN_x / 36° YX $LiTaO_3$ Structure

Alexandru C. Fechete, Wojtek B. Wlodarski, Kourosh Kalantar-zadeh, Anthony S. Holland, and
Anurat Wisistsora-at

***Abstract*—Monitoring of air-quality it is a major task nowadays as the emission of pollutant gases increases particularly in urban areas. Ozone (O_3) is a significant toxic pollutant and presents health risks. We have developed ozone sensors using a Surface Acoustic Wave (SAW) based devices. The sensors structure consists of a lithium tantalate piezoelectric ($LiTaO_3$) substrate with silicon nitride (SiN_x) intermediate layer deposited by R.F. magnetron sputtering and E-beam evaporation techniques. A 100 nm thin film of indium oxide (InO_x) deposited by R.F. magnetron sputtering provides the selectivity towards O_3. This paper presents a comparative study of the sensors performance in terms of response time, recovery time and response magnitude as a function of operational temperature. Exceptionally large frequency shift as high as 56 kHz was observed for O_3 concentrations as low as 50 parts per billion (ppb) in air. Microstructural characterization of the InO_x thin films by Atomic Force Microscopy (AFM) is also presented.**

***Index Terms*— Indium oxide, Ozone, SAW sensors, Silicon nitride.**

I. INTRODUCTION

OZONE is a strong , clean disinfectant and deodorizing agent. On the other hand ozone (O_3) is a highly reactive pollutant, toxic gas that presents health risks [1]. The analytical instruments used to detect O_3 are based on techniques such as: optical spectroscopy, gas chromatography, and mass spectrometry. These are bulky, expensive and not suitable for multispot (outdoor) measurements [2]. Therefore, compact, reliable and cheap gas sensors, which can be used for field measurements under different environmental conditions, can be an efficient alternative. Employing a Surface Acoustic Wave (SAW) based device as a gas sensor presents distinctive advantages, such as: low cost, high sensitivity and reliability [3]. They can be interfaced with electronic circuits making them portable to be used for field measurements under different environmental conditions. Among them layered the SAW devices provide a higher mass and conductometric sensitivity comparing with their non-layered SAW counterparts. Takada reported in 1993 for the first time a conductometric O_3 sensor using an indium oxide (In_2O_3) thin film [4]. Indium oxide has a unique combination of electrical and optical properties, which makes it an important material for optoelectronic and chemical sensing applications. In a non-stiochiometric form is a highly conductive semiconductor material and presents excellent sensing properties towards reducing and oxidizing gases such as hydrogen (H_2) and O_3 [5], [6]. Different deposition techniques e.g.: spin coating, spray pyrolysis, sol-gel method, and DC sputtering were used to enhance the sensitivity of In_2O_3 thin films to O_3 [6] - [8]. The sputtering methods are the most used ones as these techniques gives the best results, producing films that are mechanically stable and with good adhesion [9]. The sol-gel method produced highly dispersed In_2O_3 films with a prominent deviation from stoichiometry. Furthermore Gurlo *et al.* [10] correlated the sensing properties of the In_2O_3 films to the grain size distribution and morphology of the sol-gel prepared films. Korotcenkov *et al.* [11] reported that In_2O_3 porous films with minimal grain sizes and maximal deviation from stoichiometry have both maximal responses to O_3 and a fast response time. Doping In_2O_3 films with molybdenum and nickel ions further increases the dispersity and deviation from the stoichiometric composition [12]. Kiriakidis *et al.* [13] developed a low temperature sensor for O_3 and NO_2 gases using a dc sputtered InO_x thin film, capable of detecting 50 ppb concentrations of O_3 at 50° C. More recently ultra-sensitive low temperature O_3 and NO_2 sensors were reported using dc magnetron sputtered InO_x thin films [14]. In this paper layered SAW based ozone sensors with an InO_x / SiN_x / 36°YX $LiTaO_3$ structure are presented. The interaction of the O_3 molecules with the InO_x sensing layer perturbs the electrical boundary conditions at the surface of the SAW device. Changes in the oscillation frequency of the sensor can be correlated to the corresponding O_3 concentrations. The sensitivity of InO_x films can be attributed to the oxygen vacancies in the films. The O_2 molecules diffuse into the pores of the films to be oxidized on the surface and as a result a conductivity change of the InO_x film will take place. By controlling the oxygen deficiency, the conductivity of InO_x films can be altered [15], [16]. Silicon nitride thin film (SiNx) presents advantages for SAW device applications such as: have a high acoustic velocity, low propagation loss, high

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A.C. Fechete, W.B. Wlodarski, and K. Kalantar-zadeh are with the Sensor Technology Laboratory at the Electrical & Computer Engineering Department, RMIT University, Melbourne 3001, Victoria, AUSTRALIA (Corresponding author's tel: +61 3 99253690; fax: +61 3 99252007, e-mail: alex.fechete@ieee.org).

A.S. Holland is with the Electrical & Computer Engineering Department, RMIT University, Melbourne 3001, Victoria, AUSTRALIA (e-mail: anthony.holland@rmit.edu.au).

A. Wisistsora-at is with the National Electronic & Technology Centre, Pathumathani, THAILAND (e-mail: anurat.wisitsoraat@nectec.or.th).

temperature stability and a high wear resistance [17], [18]. Plasma Enhanced Chemical Vapour Deposited (PECVD) SiN_x have been already used on a lithium niobate ($LiNbO_3$), $LiTaO_3$ and gallium arsenate (GaAs) substrates for SAW device applications by [19], [20]. A comparative study of the performance of these ozone sensors are presented in this paper in terms of response time, recovery time and response magnitude as a function of operational temperature. The films structure, electrical and gas sensing properties is also investigated and correlated.

II. EXPERIMENTAL PROCEDURE

A. Fabrication

Layered single delay line SAW transducers were fabricated on 0.5 mm thick 36° Y-cut X-propagating $LiTaO_3$ substrate. The fabricated devices consisted of a single two-port delay line with 64 input and output interdigital electrodes with a periodicity of 24 µm. SiN_x layers with thickness of 1 µm were deposited by either RF magnetron sputtering or E-beam evaporation techniques. A 100 nm thin film of InO_x as sensing layer was deposited by RF magnetron sputtering for each sensor using the same deposition conditions. The RF magnetron sputtering technique was used as this provides good film uniformity, excellent adhesion, good thickness control and it is less expensive than other deposition methods. The SAW structure and a detailed account of the deposition parameters for the RF magnetron sputtered SiN_x and InO_x films are described in [21].

The SiN_x films were deposited by E-beam evaporation of compressed Si_3N_4 powder with 99.9 % purity. The structures were clean with oxygen-ion beam before electron beam evaporation to ensure excellent adhesion. The deposition process was conducted at the rate of ≈0.8 nm/s for 21 minutes and the substrate temperature was kept constant at 130° C. The resulting film thickness was confirmed to be ≈1 µm by Dektak Profilometer.

B. Micro-structural Characterization

The surface morphology of the films was examined by Seiko's Atomic Force Microscope (AFM) model SPA400. The scanning probe used was a Si_3N_4 microtip with ≈10 nm radius curvature. The surfaces were characterized by means of the excursion peak-valley registered in the scanning area (Zr). The average roughness (Ra), relative to a reference central plane, and a standard deviation of the z values (rms) within the given area were then estimated from the surface profile.

C. Gas Sensing Measurements

The single delay line SAW sensor was mounted on a micro-heater in a gas cell. This was connected as a positive feedback element with an amplifier to form an oscillator and was placed in a Teflon-based chamber. The heater is controlled by a regulated DC power supply providing different operating temperatures. A quartz tube exposed to UV radiation from a pen-ray type UV lamp, through which a flow of air is forced, was used to generate O_3. The sensors were exposed to different O_3 concentrations between 25 and 100 parts per billion (ppb) in the operating temperature range of 22° - 310° C. Certified gas bottles with balanced synthetic air were used at a constant flow rate of 0.200 liters per minute. Synthetic air was used to stabilize the sensor before exposure at each operating temperature. The responses were recorded as a change in the operational frequency at different operating temperature. To record the oscillation frequency of the frequency counter (Fluke PM6680B) a Lab View based program was developed.

III. RESULTS AND DISCUSSION

When the SAW sensor is exposed to an oxidizing gas such as O_3, the conductivity of the InO_x film is decreased resulting in an increase of the acoustic wave velocity. This change can be observed as an increase in the oscillation frequency. The sensitivity of InO_x films can be attributed to the oxygen vacancies in the films. By controlling the oxygen deficiency, the conductivity of InO_x films can be altered. A chemisorption of the oxygen molecules will take place on the surface of the film. After the absorption of the O_3 a reaction between the oxygen and ozone molecules will result in desorption of the reactant gas. This process of forming oxygen vacancies can be described by the following equation [16]:

$$O_o = V_o + 2e' + \tfrac{1}{2} O_2\ (\text{gas}) \qquad (1)$$

where V_o are the oxygen vacancies.

From equation (1) it can be seen that the formation of oxygen vacancies will lead to the formation of free electrons. This process of delivering free electrons between the gas and semiconductor represent the gas sensitivity.

A. Micro-Characterization Analysis

Fig. 1 shows the AFM images for the 100 nm InO_x thin film for a surface area of (25 µm x 25 µm) on the interdigital electrodes (Fig. 1a) and for (1 µm x 1 µm) surface area on the 36° YX $LiTaO_3$ substrate (Fig. 1b), respectively. It can be seen from these images that the films present a uniform distribution of nanostructured morphology. The mean grain diameter and rms surface roughness of the InO_x film were determined from the cross-section AFM image (Fig. 2) to be ≈130 nm and ≈6.5 nm, respectively.

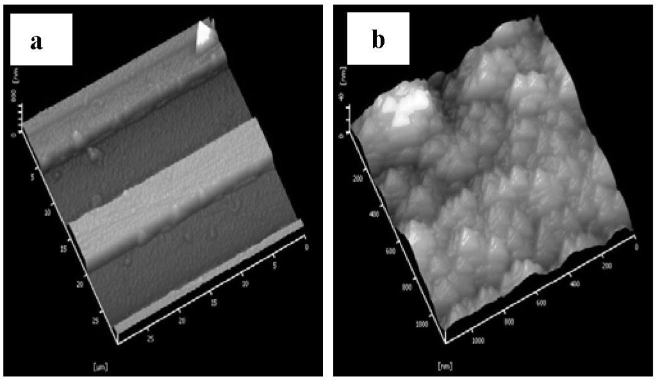

Fig. 1. AFM surface images of 100 nm InO_x thin film of an area of: (a) (25 µm x 25 µm) on the interdigital electrodes, (b) (1 µm x 1 µm) deposited on the 36° YX $LiTaO_3$ substrate.

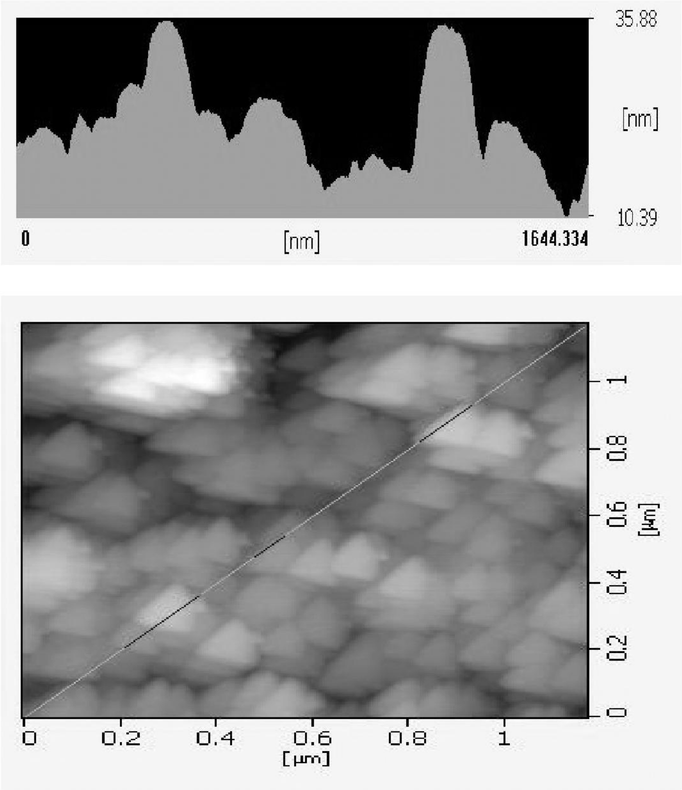

Fig. 2. AFM surface images of 100 nm InO_x thin film. The area shown is (1 µm x 1 µm).

The X-ray Photoelectron Spectroscopy (XPS) analysis performed by the authors previously on the RF sputtered InO_x films [22] revealed a good stiochiometry and an atomic ratio of (In/O) ≈ 1 through the whole thickness of the film.

B. Gas Sensing Analysis

In Fig. 3 and 4 can be seen the sensors responses towards O_3 concentrations of 25 and 50 ppb. Both sensors exhibit good performance characteristics such as: reversibility and reproducibility with stable responses. The sensor with the RF magnetron sputtered SiN_x intermediate layer has the highest sensitivity at the optimal operating temperature of 190° C, when frequency shifts of 5.0 kHz for 25 ppb and 6.5 kHz for 50 ppb concentrations of O_3 were recorded. The 90% response and recovery times were around 120 and 150 seconds, respectively. The operational temperature range of the sensor is between 185° C and 205° C [21].

In the case of the sensor with the E-beam evaporated SiN_x intermediate layer the highest sensitivity was recorded with frequency shifts of 22 kHz for 25 ppb and 56.3 kHz for 50 ppb of O_3 at the operating temperature of 245° C. The 90% response time for this SAW sensor it is around 260 seconds and the recovery time is approximately 120 seconds.

The SAW sensor with the E-beam evaporated SiN_x intermediate layer exhibits a higher sensitivity (Fig. 5.). The magnitudes of the responses are almost 8 times higher than of the sensor with the RF magnetron sputtered SiN_x middle layer.

Sputtered and evaporated films generally have different surface morphology, as the sputtered surfaces are usually rougher. Therefore it is believed that differences in the sensors fabricated here can be correlated to the differences in surface morphology and stoichiometry of the SiN_x film deposited by the two techniques.

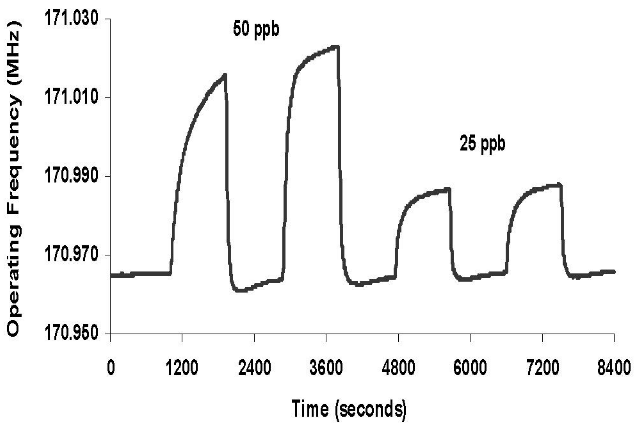

Fig. 3. The dynamic response of the layered SAW sensor with E-beam Evaporated SiN_x intermediate layer at the operating temperature of 245° C.

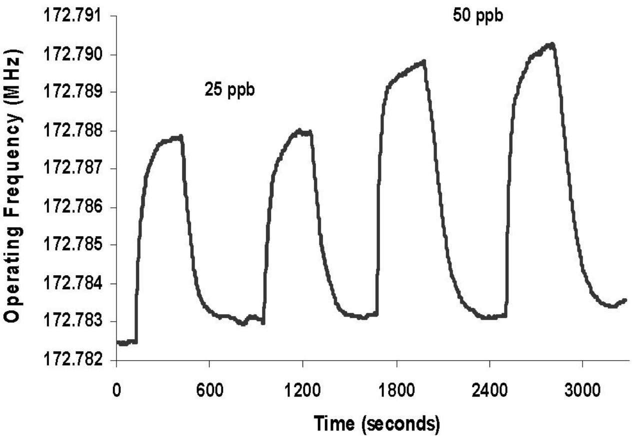

Fig. 4. The dynamic response of the layered SAW sensor with RF magnetron sputtered SiN_x intermediate layer at the optimal operating temperature of 190° C.

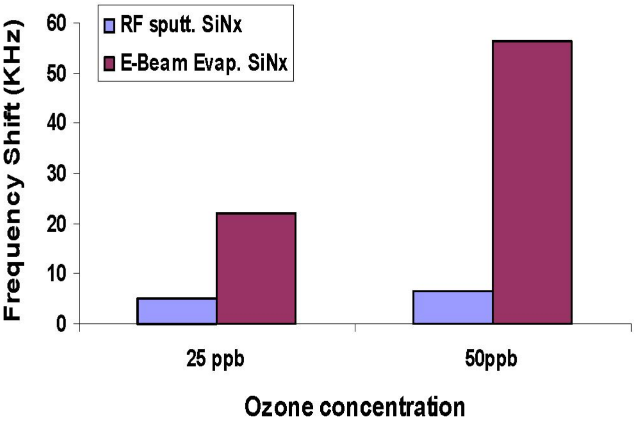

Fig. 5. Frequency shifts of the SAW sensors for different O_3 concentrations.

IV. CONCLUSION

SAW based O_3 sensors have been fabricated using RF magnetron sputtering and E-beam evaporation techniques for the deposition of the SiN_x intermediate layer. The InO_x sensing layer in both cases was deposited by RF magnetron sputtering. The sensors showed stable, sensitive and repeatable gas sensing characteristics. However the sensor with the E-beam evaporated SiN_x exhibited a much higher sensitivity. We are currently improving the InO_x / SiN_x films dynamic characteristics by analyzing the surface morphology and stoichiometry of the deposited films. The presented results clearly demonstrate that these sensors are promising for gas-sensing applications, employed as SAW based O_3 sensor for low ppb range. Further work is needed also for the optimization of the thicknesses of the InO_x / SiN_x films.

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Alexandru C. Fechete received his Bachelor of Communication Engineering from RMIT University, Melbourne, Australia, in 2002. He became a Member (M) of IEEE in 2003 and he is currently working towards a PhD degree with the Sensor Technology Group at RMIT University, Melbourne. His area of research is in gas sensing, investigating metal oxide nanocrystals for gas sensing applications, concentrating on Surface Acoustic Wave (SAW) based gas sensors.

Wojtek Wlodarski has worked in the areas of sensor technology and instrumentation for over 30 years. He has published four books and monographs, over 250 papers and holds 28 patents. He is a Professor at RMIT University, Melbourne, Australia, and heads the Sensor Technology Laboratory located at the School of Electrical and Computer Engineering.

Kourosh Kalantar-zadeh received his Bachelor of Science and Master of Science from Tehran University, Tehran, Iran and Sharif University of Technology, Tehran, Iran, respectively. He received his PhD from RMIT University, Melbourne Australia in 2002. Kourosh is a lecturer at RMIT University, Melbourne, Australia. He is currently undertaking a research on surface acoustic wave (SAW) biosensors under the CRC for micro-technology funding. His previous research and development involvements include: SONAR systems, MRI signal processing and ionospheric surveillance systems. He has published more than 30 scientific papers in refereed journals and in the proceedings of international conferences and holds two patents.

Anthony S. Holland received the B.A.I. degree in electronics from Trinity College, Dublin, Ireland, in 1987, and the M.Eng and Ph.D. degrees from Royal Melbourne Institute of Technology (RMIT) University, Melbourne, Australia, in 1995 and 1999, respectively. From 1999 to 2002, he was a Research Associate at RMIT investigating diamond films used for surface acoustic wave devices. Since 2002 he worked as a Research Fellow at RMIT on photonics devices. Currently he is a lecturer in microfabrication for different technologies.

Anurat Wisitsora-at received his Ph.D., M.S. degrees from Vanderbilt University, TN, U.S.A., and B. Eng degree in Electrical Engineering from Chulalongkorn University, Bangkok, Thailand in 2002, 1997, and 1993, respectively. His research interests include gas sensors, microelectronic fabrication, semiconductor devices, electronic and optical thin film coating, sensors, micro- electromechanical systems (MEMS), and vacuum microelectronics.