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Ozone Sensors based on Layered SAW Devices with: InO$_x$ / SiN$_x$ / 36° YX LiTaO$_3$ Structure

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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 multipoint (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 (InO$_x$) 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-stoichiometric 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 InO$_x$ thin films to $O_3$ [6] - [8]. The sputtering methods are the most used ones as these techniques give the best results, producing films that are mechanically stable and with good adhesion [9]. The sol-gel method produced highly dispersed In$_2$O$_3$ films with a prominent deviation from stoichiometry. Furthermore Gurlo et al. [10] correlated the sensing properties of the In$_2$O$_3$ films to the grain size distribution and morphology of the sol-gel prepared films. Korotcenkov et al. [11] reported that In$_2$O$_3$ 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$_2$O$_3$ films with molybdenum and nickel ions further increases the dispersity and deviation from the stoichiometric composition [12]. Kiriaakis 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 $O_3$ 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 (SiN$_x$) presents advantages for SAW device applications such as: have a high acoustic velocity, low propagation loss, high

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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 consists 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$_3$N$_4$ 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$_3$N$_4$ 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$_2$ 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]:

$$\text{O}_2 = V_0 + 2e^+ + \frac{1}{2} \text{O}_2 \text{ (gas)}$$

where $V_0$ 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.
The X-ray Photoelectron Spectroscopy (XPS) analysis performed by the authors previously on the RF sputtered InO₃ films [22] revealed a good stoichiometry 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 O₃ 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 SiNₓ 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 O₃ 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 SiNₓ intermediate layer the highest sensitivity was recorded with frequency shifts of 22 kHz for 25 ppb and 56.3 kHz for 50 ppb of O₃ at the operating temperature of 245°C. The 90% response time for this SAW sensor is around 260 seconds and the recovery time is approximately 120 seconds.

The SAW sensor with the E-beam evaporated SiNₓ 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 SiNₓ 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 SiNₓ film deposited by the two techniques.

![AFM surface images of 100 nm InO₃ thin film. The area shown is (1 µm x 1 µm).](image)

![The dynamic response of the layer SAW sensor with E-beam Evaporated SiNₓ intermediate layer at the optimal operating temperature of 245°C.](image)

![The dynamic response of the layer SAW sensor with RF magnetron sputtered SiNₓ intermediate layer at the optimal operating temperature of 190°C.](image)

![Frequency shifts of the SAW sensors for different O₃ concentrations.](image)
IV. CONCLUSION

SAW based O₃ sensors have been fabricated using RF magnetron sputtering and E-beam evaporation techniques for the deposition of the SiNₓ intermediate layer. The InOₓ 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 SiNₓ exhibited a much higher sensitivity. We are currently improving the InOₓ / SiNₓ 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 O₃ sensor for low ppb range. Further work is needed also for the optimization of the thicknesses of the InOₓ / SiNₓ films.

REFERENCES


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