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Procedia Engineering 87 (2014) 999 – 1002

Procedia Engineering

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EUROSENSORS 2014, the XXVIII edition of the conference series

Graphene-coated Rayleigh SAW Resonators for NO_2 Detection

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Abstract

This paper describes the development of a novel low-cost Rayleigh Surface Acoustic Wave Resonator (SAWR) device coated with a graphene layer that is capable of detecting PPM levels of NO_2 in air. The sensor comprises two 262 MHz ST-cut quartz based Rayleigh SAWRs arranged in a dual oscillator configuration; where one resonator is coated with gas-sensitive graphene, and the other left uncoated to act as a reference. An array of NMP-dispersed exfoliated reduced graphene oxide dots was deposited in the active area inside the SAWR IDTs by a non-contacting, micro ink-jet printing system. An automated Mass Flow Controller system has been developed that delivers gases to the SAWR sensors with circuitry for excitation, amplification, buffering and signal read-out. This SAW-based graphene sensor has sensitivity to NO_2 of *ca.* 25 Hz/ppm and could be implemented in a low-power low-cost gas sensor.

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: Surface Acoustic Sensor; NO_2 detection; Graphene oxide; SAW Resonator; Dual SAW

1. Introduction

Significant research has been carried out in the development of low-cost sensors for monitoring and controlling toxic gases responsible for global pollution. Among the various toxic chemicals studied, NO_2 is one of the most dangerous pollutants that contributes to several environmental effects, such as acid rain and ozone formation and can cause health problems at very low concentrations. Due to the drastic impact of NO_2 on public health and

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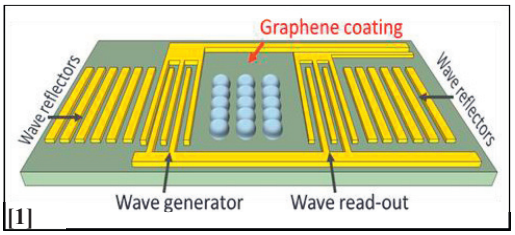
Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.328

environment, extensive research is being carried out in the field of NO_2 detection. In this paper, NO_2 detection mechanism using graphene based surface acoustic wave resonators (SAWR) is discussed. Even though SAWRs ($LiTaO_3$-based) incorporating graphene-coating have been previously used for sensing hydrogen, carbon monoxide, carbon dioxide, and ambient humidity [1], practically no work has been carried out in the detection of NO_2 gas.

We exhibit, for the first time, the response of graphene based Rayleigh SAW Resonators fabricated on quartz substrate to NO_2, as they are good candidates for monitoring changes in surface acoustic properties due to mass loading (Fig.1). The system described here is capable of demonstrating the dependence of the acoustic impedance of graphene on NO_2 in air utilizing quartz-based SAWR sensors [2]. Exfoliated reduced graphene oxide (RGO), which is not pure graphene have been used as the coating layer for the sensor. Hernandez *et al*. [3] commented that RGO is not perfect graphene but functionalized with hydroxyls and epoxides. Furthermore, Gardner *et al*. [4] confirmed the presence of defects or oxides for the graphene studied here by Raman spectroscopy.



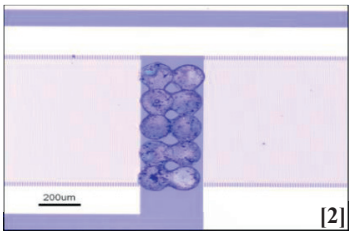


Fig. 1. Schematic of a two-port quartz-based Rayleigh SAW resonant device coated with an array of exfoliated graphene oxide micro-dots.
Fig. 2. Optical micrograph of the 262 MHz SAWR sensor coated with an array of graphene dots in *free* sensing area. Dot diameter is 150

2. Materials and Methods

2.1. SAW Resonator Design

The two-port SAWR sensors used in this work was batch fabricated on a 4" ST-cut quartz substrate wafer using UV lithography (PacTech, Germany) as explained in [2]. These dual sensors with an overall die size of 9.6 mm × 3.6 mm have a resonant frequency of 262 MHz and consists of aluminium based inter-digital-transducers (IDT), producing a Rayleigh wave in the crystallographic X-direction. Each IDT comprises a set of 60.5 finger pairs with a finger width of 3 µm and an acoustic aperture of 720 µm. A distance of 303 µm, between the input and output IDTs produce a standing wave pattern. 600 shorted reflector gratings surround each IDT with a 6 µm pitch [2]. The dual SAWR sensor (with reference channel) arrangement enables a differential operation that removes common mode variations such as temperature and humidity. Graphene was deposited on one side of each dual device (Fig.2), while the other side was left blank to act as a reference signal, in order to produce a low-noise differential signal.

2.2. Graphene ink formulation

We prepare the graphene-based printable ink as explained in [5]. Graphite flakes (NGS Naturgraphit) are sonicated (Decon bath, 100W) in NMP for 9 hours. The un-exfoliated flakes are left to settle for 10 minutes after sonication. The decanted dispersions are then ultra-centrifuged using a TH-641 swinging bucket rotor in a Sorvall WX-100 Ultra-centrifuge at 10,000 rpm (~15,000g) for an hour and filtered to remove flakes >1µm, that might clog the nozzle. The resulting ink is characterized by Optical Absorption Spectroscopy (OAS), High Resolution Transmission Electron Microscopy (HRTEM), Electron diffraction and Raman spectroscopy.

A Perkin-Elmer Lambda 950 spectrometer with 1nm resolution is used for the OAS measurements. OAS can be used to estimate the concentration of graphene [3], [5], [6] using the Beer-Lambert Law according to the relation $A=\alpha cl$, where A is the absorbance, l [m] is the light path length, c [g/L] the concentration of dispersed graphitic material and α [L g-1m-1] the absorption coefficient.

From α~1390Lg-1m-1 at 660nm [6], [7] and measured A~0.8, we estimate c~0.11±0.02g/L. A combination of HRTEM and Raman Spectroscopy analysis showed that the graphene-ink mostly consists of SLGs, Bi-Layers (BLG) and FLGs, with lateral size~300-1000nm. We find that ~35\% SLGs are larger than 300nm; ~40\% BLGs are larger than 350nm; ~55\% FLGs are larger than 450nm. In particular, we have 33\% SLG with c~0.11g/L [5].

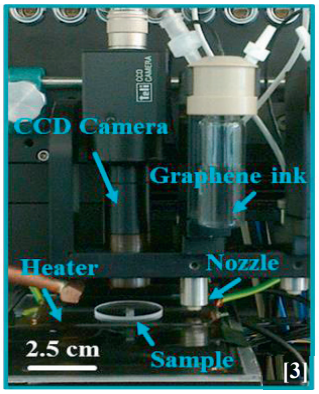


Fig. 3: Photograph of micro inkjet deposition system along with SAWR sample.

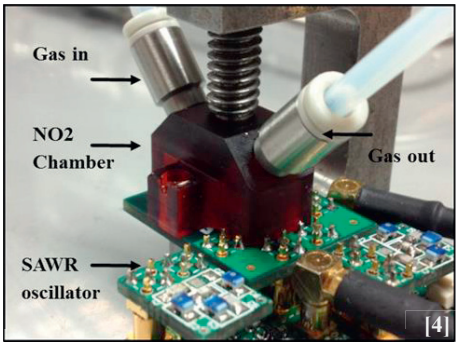


Fig. 4: The experimental setup for the detection of NO_2 vapour, showing the gas chamber with the in/out openings, placed over the SAWR oscillator system.

2.3. Graphene Deposition

Graphene was deposited onto the *free* sensing area of the SAWR sensor. A matrix of 2×5 dots (*ca*. 120um diameter with a centre-to-centre spacing of 200 μm) of NMP-dispersed exfoliated graphene was deposited by micro ink-jet printing as shown in Fig. 3. (Microdrop Tech.). The system is fitted with (i) a PC controlled stage and a CCD camera, which guarantees very accurate positioning of the sample under the ink dispensing nozzle; (ii) a strobe monitoring unit used to verify in time the drop stability and the absence of satellites drops, which might be responsible for a detrimental worsening of the process reproducibility; (iii) an in-house built heater, used to raise the temperature of the sample above ambient temperature (approx. 80ºC) [4] in order to control the dimension of the deposited dots. A script for automatic dispensing of the ink in predefined location of the sample was realized. 500 drops of graphene ink were dispensed for a total of roughly 50 nL for each dot and a deposition time of approx. 10 minutes.

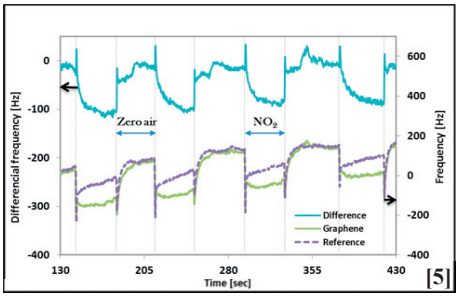
2.4. Experimental

The experimental setup for vapour detection using a graphene-SAWR device is shown in Fig. 4. The gas delivery system comprises high purity gas cylinders equipped with regulators and safety shut-off valves, inline particle and moisture filters, high-precision digital mass flow controllers to set the required gas concentrations to the sensor and inline check valves to prevent reverse gas flow. A gas chamber comprising of inlet and outlet holes, is attached to the sensor board, which allows the NO_2 gas mixture at various concentrations (ppm levels) to interact with the graphene layer coated on the sensing area. The gas mixture had a constant flow rate, and zero grade air was used as the reference (baseline) gas. These sensors resonate in a feedback loop of a simple RF oscillator circuit containing a high gain amplifier and a buffer with a low-pass filter in order to suppress oscillations at unwanted frequencies. The oscillation frequency of the SAWR oscillator circuit was recorded using a commercial instrument (JLM Innovation, Tubingen, Germany).

3. Results

The electro-acoustic interaction of NO_2 on graphene has been demonstrated as a frequency response of the SAWR sensors. On the binding of NO_2 molecules with graphene-SAWR, the oscillation frequency of the resonator decreases, which will be measured and recorded as a differential signal. The typical frequency output (Fig. 5) of a dual SAWR to four subsequent injections of 3 ppm NO_2 in air shows that the sensor response is fast, reproducible

and low noise. In a similar manner, the frequency response of the graphene-coated SAWR sensors was measured to various levels of NO2 concentrations to establish the minimum sensitivity of the sensors. The relationship between the graphene-SAWR sensitivity and NO_2 concentrations has been established to be approx. a log-linear response (Fig. 6), which modelled the sensor response linearly with volatile concentration confirming to have the sensor to be operating in the non-saturated regime.



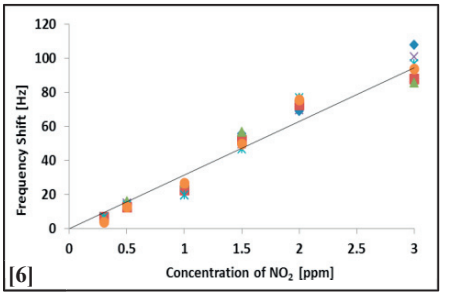


Fig. 5: Typical frequency output of a dual SAWR sensor in response to sequential injections of 3 ppm of NO_2 in air. Fig. 6: Linear frequency response of graphene SAWR sensor towards different low concentrations of NO_2 gas in air.

We believe that the defects in graphene oxide produced a higher sensitivity to reactive gases, such as NO_2. The extent of the surface acoustic wave penetration into the adjacent medium (exfoliated graphene oxide layer) determines the frequency change to the detected NO_2 concentration. In general, the frequency response, 'f' of a graphene-SAW sensor is given by $f = kc^n$ where k is the sensitivity constant, the exponent n is close to unity, and c is the concentration of reactive gas. Thus the sensitivity k of the graphene-SAWR is given by $\Delta f/\Delta c \approx 25$ Hz/ppm.

4. Conclusion

In conclusion, we have presented a novel grapheme-based SAWR sensor system, capable of detecting sub-ppm levels of NO_2. We believe that our SAWR based gas sensor can be used a sensitive, selective, low-power and low-cost gas sensor. In addition, sensitivity can also be improved by using an ultra-thin exfoliated graphene oxide layer with thicknesses comparable to the SAWR radiation depth. However, it has been identified that these sensors have cross sensitivity to water vapour, resulting in sensitivity degradation. Further studies are being carried out in the detection of other reactive gases (e.g. CO) and their cross-sensitivities. The integration of graphene with Rayleigh wave sensors could form a revolution in low-cost low-power chemical and environmental applications.

Acknowledgements

The authors thank Mr F. Courtney (University of Warwick) for the fabrication of the gas sensing chamber.

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