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SAW Gas Sensors with Carbon Nanotubes Films

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***Abstract*—A surface acoustic wave (SAW) gas sensor with multiwalled carbon nanotubes (CNTs) layered films as chemically interactive nanomaterial is presented. A SAW two-port resonator integrated on ST-cut quartz substrate has been functionally characterized as oscillator in dual differential mode at the resonant frequency of 433.92 and 915 MHz. Nanocomposite layers based on filler of CNTs, grown by RF-plasma enhanced chemical vapor deposition, have been prepared by the Langmuir-Blodgett (LB) technique to coat the SAW microdevices for organic vapor detection, at room temperature. Results concerning the SAW sensing performance towards ethanol, methanol, acetone, m-xylene, and toluene are described. These results demonstrate clearly the potential of the SAW CNTs-nanocomposite chemical microsensors at high frequencies for the fabrication of low-cost and highly gas-sensitive devices for promising room-temperature sensing operations.**

Keywords-components: SAW gas sensors; Carbon nanotubes; Langmuir-Blodgett films; Nanocomposite; SAW resonators

I. INTRODUCTION

Surface acoustic wave (SAW) sensors have been widely investigated [1-4] and advantageously used to monitor gas and vapor concentration for detecting hazardous compounds in gaseous and/or liquid phase sensing applications. If the SAW devices are coated by a sensitive material that selectively adsorbs target analyte molecules, the output signal of the SAW transducer results to be proportionally correlated to the concentration of the chemical measurand. In this context, the nanomaterials appear to be very promising as chemically interactive materials for SAW gas devices [5]. A class of sensor nanomaterials with interesting physical properties of high surface area, hollow structure and chemical reactivity are the carbon-based nanostructures, mostly carbon nanotubes (CNTs) both in the singlewalled and multiwalled structure. Nanocomposites with CNTs-filler in organic host-matrix have been prepared by Langmuir-Blodgett (LB) technique as nanosized molecular films with tailored content in weight-ratio of CNT-filler for gas detection, at room temperature [6,7]. Here, new challenges are tackled including high sensitivity, sub-ppm level gas detection, low noise and high resolution, at room temperature. The SAW devices are typically configured as delay lines or port-resonators with a pair of input and output interdigital transducers (IDTs) to launch and receive an acoustic wave. In the case of resonators, a set of metal strips located externally to the IDTs at both ends of the planar piezosubstrate, acts as acoustic reflectors of a resonant cavity. The resonators are narrower band at high Q-factor and usually more stable than delay lines. They usually operate in the frequency range from 200 MHz to 1-2 GHz. One commonly inserts either a delay line or a resonator into a feedback loop of an oscillator whose frequency output depends on the mass adsorbed into coating, hence on gas concentration of molecules adsorbed. Furthermore, the frequency shift depends on the squared fundamental frequency of the SAW oscillator, in the case of mass-loading only. Thus, the mass sensitivity increases with the resonating frequency. The main objective of this work is to experimentally demonstrate that the high-frequency SAW 433.92 and 915 MHz two-port resonators functionalized with LB films of CNTs-based nanocomposites are suitable for high-performance detection of volatile organic compounds of alcohols, ketones, aromatic compounds, at room temperature.

II. THEORY

Generally, the mass sensitivity in the SAW devices-based oscillators is defined as the incremental frequency change in response to an incremental change in the mass per unit area on the SAW sensor surface. The effect of a thin nonconducting layer of thickness h and density ρ on the resonant frequency of a SAW device can be described [8,9] as follows:

$$\Delta f = -c_m f_o^2 \Delta\rho_s + c_e f_o^2 \Delta[hG'] - \frac{K_t^2}{2}\Delta\left[\frac{\sigma_s^2}{\sigma_s^2 + v_o^2 C_o^2}\right] \quad (1)$$

where, Δf is frequency shift, c_m mass sensitivity coefficient, c_e elasticity sensitivity coefficient, f_o fundamental SAW frequency, Δm mass change, A area of the SAW sensing membrane, ρ_S density of the adsorbent phase, G' real part of the shear modulus, K_t^2 electromechanical coupling factor, v_0 unperturbed SAW velocity, σ_S sheet conductivity of the sensing film, C_0 capacitance per unit length of SAW substrate, $C_0 = \varepsilon_S + \varepsilon_0$, with ε_S permittivity of substrate, ε_0 permittivity of free space. The three terms of the equation (1) indicate the contributes of the changes in mass (mass loading), changes in viscoelastic constants (viscoelastic loading), and changes in electrical conductivity (acoustoelectrical loading), respectively.

For a SAW device affected by mass loading only, the gas response of the mass-sensitive sensor is well-known written as:

$$\Delta f = c_m f_o^2 \frac{\Delta m}{A} \quad (2)$$

As noted, the frequency shift increases with the squared resonant frequency, thereby the SAW gas response of mass-sensitive devices improves with the operating frequency, for a given surface density. Generally, also the noise increases with the frequency, therefore a trade-off between gas sensitivity and signal-to-noise ratio should be addressed at higher frequencies.

The gas sensitivity of a SAW device coated with a gas-sensitive layer is determined primarily by the coating thickness, the partition coefficient, and changes in the physical properties of the coating caused by gas adsorption. When the SAW gas response is gravimetric, then the frequency shift depends linearly on vapor concentration and can be written as follows:

$$\Delta f_V = \Delta f_M C_V \frac{K}{\rho_S} \tag{3}$$

where K is the partition coefficient, $K = C_S/C_V$, with C_S concentration of vapor in the sorbent phase, C_V concentration of vapor in the vapor phase, Δf_V is frequency shift due to mass loading of the gas molecules adsorbed, Δf_M is frequency shift caused by deposition of the adsorbent phase onto the device surface. Thus, the SAW frequency shift due to the mass of gas sorbed is a function of the amount of the deposited coating expressed as a frequency shift. Hence, the SAW gas response in a nanocomposite layer can be tuned by changing the weight-content of the CNTs-filler because both the partition coefficient and surface density of the layer are simultaneously modified.

III. Experimental Details

A. Growth of Carbon Nanotubes

The multiwalled CNTs have been used as filler in the nanocomposite film. The CNTs have been grown by Radio Frequency Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) technology onto dielectric alumina substrate coated by Cobalt catalyst nanoclusters, prepared by sputtering, with a nominal thickness of 6 nm. The plasma in the RF-PECVD growth reactor was constituted by a C_2H_2/H_2 (20/80 sccm) gas mixture. The process parameters for growing CNTs were set at a rf power (13.56 MHz), working pressure, and temperature of 100 W, 1.5 Torr, and 450°C, respectively. Experimental details on growth are reported elsewhere [10]. A deposition time of 30 minutes was used to grow a CNTs networked layer whose nominal thickness was estimated as 250-300 nm. The diameter of the tangled bundles of the multiwalled CNTs varied in the range from 5 to 30 nm. Their length ranges from 0.1 to 10 μm.

B. CNTs-Nanocomposite Langmuir-Blodgett Films

The deposition of the CNTs-based nanocomposite films was carried out by Langmuir-Blodgett (LB) technique using a Langmuir trough (KSV 5000). The Y-type LB cadmium arachidate (CdA) was used as host-matrix due to peculiar molecular structure and suitability for LB processing. Two types of solutions were prepared to fabricate the nanocomposite with different CNTs-filler weight-ratio content of 10 and 50 wt.%: a *solution A* of arachidic acid in chloroform and a *solution B* of CNTs in chloroform. These two solutions were mixed, dispersed, and stirred in an ultrasonic bath. Then, this mixed solution was spread onto the LB subphase of deionized water (18 MΩ) containing 10^{-4} M $CdCl_2$ as well. The subphase pH was 6.0 and the temperature was 19°C. The nanocomposite monolayer was compressed with a barrier rate of 15 mm/min up to a surface pressure of 27 mN/m. The dipping rate was of 14 mm/min. The transfer ratio of the monolayer from subphase to SAW device surface ranged from 0.6 to 0.7. Experimental details on LB film preparation are reported elsewhere [11]. A LB nanocomposite film of 2 monolayers of CNTs embedded into the CdA host-matrix with 10 and 50% of weight-ratio were deposited onto the SAW 433.92 and 915 MHz quartz substrates. A typical frequency shift (insertion loss change) for a SAW 433.92 MHz quartz resonator coated by 2-monolayers of 10 and 50 wt.% CNTs-CdA nanocomposite was of 169.8 kHz (13.1 dB) and 163.5 kHz (11.4 dB), respectively.

C. SAW Devices

Commercially available SAW ST-cut,X-propagation quartz two-port resonators (433.92 MHz, ISM Filter model, Temex; 915 MHz, RP1094 model, RFM) are used as passive acoustic elements. The devices at 433.92 MHz are configured as transversely-coupled double 1-port resonator filters with a frequency of symmetric and antisymmetric mode, as reported in Fig. 1, while the devices at 915 MHz are designed as simple two-port resonators with two IDTs arranged between reflecting gratings. These two-port resonators are mounted on 3-pin round TO-39 package. The sizes of the SAW 433.92 MHz resonators are 4.0 mm length x 1.0 mm width x 0.5 mm thickness. The sizes of the SAW 915 MHz resonators are 2.0 mm length x 1.0 mm width x 0.5 mm thickness. The period of the SAW 433.92 and 915 MHz resonators was of 7.2 and 3.4 μm, respectively. A typical curve of the S_{21} characteristic (logmag and phase) for unloaded SAW 433.92 MHz ST-quartz resonator is shown in Fig. 2.

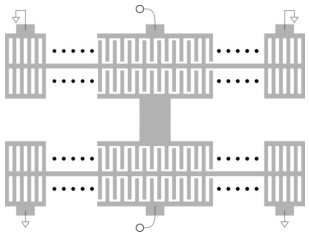

Figure 1. Scheme of a SAW transversely-coupled double 1-port resonator filter implemented on ST-quartz with frequencies of 433.92 MHz.

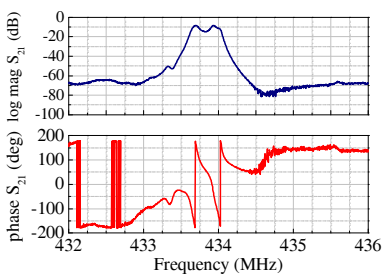

Figure 2. S_{21} parameter (logmag and phase) of a SAW 433.92 MHz two-port resonator fabricated on ST-quartz substrate.

The high Q (> 2500) and low insertion loss (< 15 dB) make these devices quite stable when inserted as frequency-control element in a properly-designed oscillator (Pierce oscillator for SAW 433.92 MHz device; Colpitts modified-oscillator for SAW 915 MHz device) implemented by SMD components onto PCB including a low-noise and high-gain RF-amplifier. The scheme of the SAW-based oscillator is shown in Fig. 3.

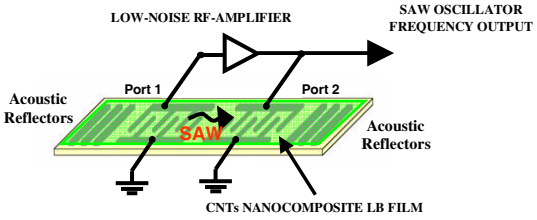

Figure 3. Scheme of the SAW sensor oscillator.

The gas exposures measurements were performed at room-temperature in dual differential configuration with two SAW oscillators: one Sensor coated by gas-sensitive layer and other Reference bare without any coating. The difference frequency is proportionally related to gas concentration under test with the advantages of rejection for common-mode error-sources to lower the effects of interfering parameters such as temperature and humidity on SAW gas response. A typical scheme of the SAW dual sensor system is shown in Fig. 4. Dry air was used as reference and carrier gas for transport the target organic vapors of ethanol (10-100 ppm), methanol (40-130 ppm), acetone (150-500 ppm), m-xylene (10-30 ppm) and toluene (20-80 ppm) in the cell test containing the SAW sensor dual system. The bubbling method was used to generate the tested vapors by mixing the dry and saturated streams to control the concentration desired.

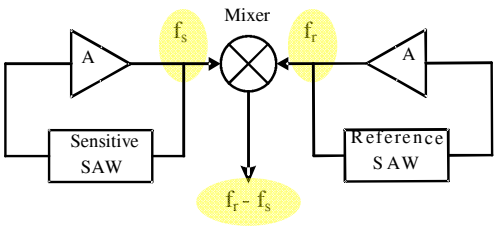

Figure 4. Scheme of SAW sensor oscillator in differential configuration.

IV. Results and Discussion

Fig. 5 shows the time response of the dual SAW 433.92 MHz device consisting of an uncoated SAW reference and a SAW sensor coated with a 10 wt.% CNTs-CdA nanocomposite LB film to pulses of low concentrations of ethanol, at room temperature. The SAW reference changes its frequency due to sticking of gas molecules onto bare surface of the SAW quartz substrate, while the SAW sensor modulates its frequency response due to gas adsorption by LB film and finally, the SAW difference frequency changes upon exposure of gas concentration without the interfering effects of the surrounding influences (e.g., temperature, humidity). The calibration curve of the SAW difference change as a function of the ethanol concentration is shown in Fig. 6. A non-linear relationship has been measured in the whole tested concentration range. This demonstrates that the mass-loading effect is not the unique contribute to the SAW response and other effects as the viscoelastic loading and the acoustoelectrical loading should be considered as well, as theoretically reported in equation (1).

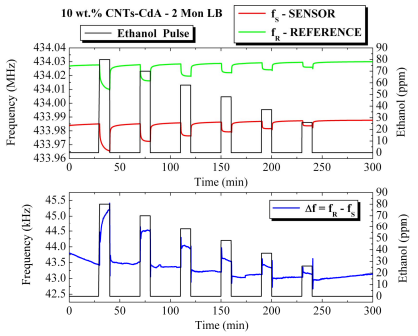

Figure 5. Room-temperature time response towards ethanol of the dual SAW 433.92 MHz device with uncoated SAW Reference and SAW Sensor element coated by a 2-monolayer thick 10 wt.% CNTs-CdA LB nanocomposite. The frequency difference is reported in lower track.

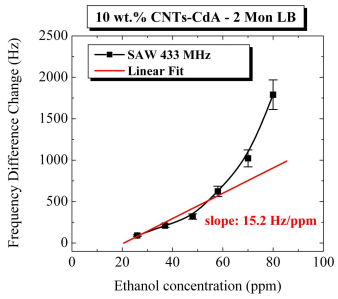

Figure 6. Room-temperature calibration curve in terms of frequency difference change to ethanol of the dual SAW 433.92 MHz device with Sensor element coated by 2-monolayer thick 10 wt.% CNTs-CdA LB nanocomposite.

Fig. 7 shows the chemical patterns in terms of mean sensitivity (frequency shift weighted over unit concentration) towards ethanol, methanol, toluene, m-xylene, acetone, at room temperature. The dual SAW sensor-system shows the highest sensitivity towards ethanol, then to tested alcohol of methanol, next to acetone and finally a very low sensitivity to aromatic hydrocarbons of toluene and m-xylene. Thus, pronounced selectivity to alcohols, especially ethanol, is measured.

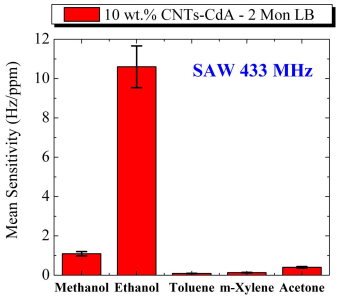

Figure 7. Room-temperature chemical patterns of mean sensitivity towards methanol, ethanol, toluene, m-xylene and acetone of the dual SAW 433.92 MHz sensor with SAW Sensor element coated by a 2-monolayer thick 10 wt.% CNTs-CdA LB nanocomposite film.

Fig. 8 shows a comparison of the chemical patterns in terms of mean sensitivity for a dual SAW device using a LB nanocomposite film based on a 10 wt.% CNTs-CdA coating, at 433.92 and 915 MHz. As shown, the SAW sensitivity increases with higher frequency, as theoretically reported in equation (2). This can be attributed to surface effects of the gas adsorption in the very thin LB layer. Hence, thin sensing LB layers are useful to improve the gas sensitivity of the SAW devices with higher resonant frequency. Furthermore, the ratio of the mean sensitivity of the SAW devices at 915 and 433.92 MHz, $S_{M\ 915\ MHz}$ / $S_{M\ 433\ MHz}$, is measured as 7.12 for ethanol, against the squared frequencies ratio, $(f_1/f_2)^2$, of 4.46. The comparison, related to these unbalanced values, confirms that the mass-loading is not the unique contribute to the SAW response for ethanol. In the contrast, for methanol, the ratio of the mean sensitivity of the two SAW devices at the different frequencies is 4.28, against the squared frequencies ratio of 4.46. These comparable values demonstrate that the mass loading could be the dominant sensing mechanism for methanol detection.

Fig. 9 shows the room-temperature transient response of the frequency difference for a SAW 915 MHz device coated with 10 and 50 wt.% CNTs-CdA LB nanocomposite. The sensitive coating with different weight-ratio of CNT-filler in the LB nanocomposite affects the SAW gas response changing the partition coefficient and the surface density, as theoretically reported in equation (3). The SAW ethanol sensitivity is higher for larger content of 50 wt.% weight-ratio of CNT-filler caused by higher gas adsorption of larger CNT-filler content.

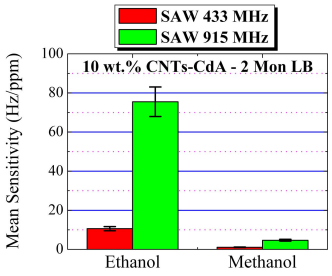

Figure 8. Comparison of the room-temperature chemical patterns in terms of mean sensitivity towards ethanol and methanol for the dual SAW 433.92 and 915 MHz sensor with the Sensor element coated by a 2-monolayer thick 10 wt.% CNTs-CdA LB nanocomposite film.

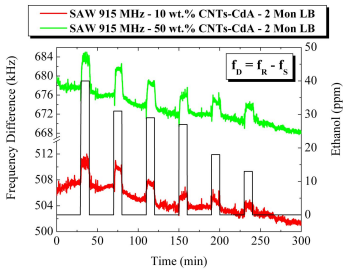

Figure 9. Room-temperature time response to ethanol of the dual SAW 915 MHz device with uncoated SAW Reference and SAW Sensor element coated by a 2-monolayer thick 10 wt.% and 50 wt.% CNTs-CdA LB nanocomposite.

V. Conclusions

Microacoustic SAW two-port resonator sensors have been designed and fabricated onto ST-cut quartz substrates operating at frequency of 433.92 and 915 MHz. Langmuir-Blodgett films based on carbon nanotubes nanocomposite layer have been deposited onto SAW resonator as very sensitive coating for vapor sensing, at room temperature. SAW chemical sensors have been functionally characterized as oscillator resonating at 433.92 and 915 MHz in dual differential mode. SAW CNTs-nanocomposite sensors have been studied at ppm level of vapor detection below their related Threshold Limit Values (TLV), with a good selectivity towards alcohols, and particularly for ethanol. Future work is planned in the area of the LB nanocomposite processing with different weight content of CNTs-filler and different type of CNTs-filler for enhanced vapor sensitivity. Optimization of electronics design for SAW 915 MHz oscillator will be addressed. SAW gas sensor arrays with low-selective coatings based on CNTs-nanocomposite LB films will be also investigated for practical applications.

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