

## Chapter 42

# Enhanced Mass Sensitivity of Carbon Nanotube Multilayer Measured by QCM-Based Gas Sensors

M. Penza, P. Aversa, R. Rossi, M. Alvisi, G. Cassano, D. Suriano and E. Serra

**Abstract** A Quartz Crystal Microbalance (QCM) gas sensor coated with carbon nanotubes (CNTs) layered films as chemically interactive nanomaterial is described. A QCM resonator integrated on AT-cut quartz substrate has been functionally characterized as oscillator at the resonant frequency of 10 MHz. The CNTs have been grown by chemical vapor deposition (CVD) system onto alumina substrates, coated with 2.5 nm thick Fe catalyst, at a temperature of 750°C in H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> gaseous ambient as active materials for gas sensors. CNTs multilayers, with and without buffer layer of cadmium arachidate (CdA), have been prepared by the Langmuir–Blodgett (LB) technique to coat at the double-side the QCM sensors for organic vapor detection, at room temperature. It was demonstrated that the highest mass sensitivity has been achieved for CNTs multilayer onto CdA buffer material due to the greatest gas adsorbed mass. The sensing properties of the CNTs-sensors at enhanced mass sensitivity have been investigated for three different vapors of ethylacetate, acetone and m-xylene in the range of gas concentration from 10 to 800 ppm. The CNTs-based QCM-sensors exhibit high sensitivity (e.g., 5.55 Hz/ppm to m-xylene of the CNTs-multilayer) at room temperature, fast response, linearity, reversibility, repeatability, low drift of the baseline frequency, potential sub-ppm range detection limit.

---

M. Penza (✉) · P. Aversa · R. Rossi · M. Alvisi · G. Cassano · D. Suriano  
Brindisi Technical Unit for Technologies of Materials, ENEA, PO Box 51, Postal Office  
Br4, 72100 Brindisi, Italy  
e-mail: michele.penza@enea.it

E. Serra  
Casaccia Technical Unit for Technologies of Materials, ENEA, Via Anguillarese 301,  
00060, Rome, Italy

## 42.1 Introduction

Quartz Crystal Microbalances (QCMs) have been widely used as high-performance transducers and promising sensor platforms for chemical detection of targeted analytes in air [1] and/or water [2] phase. The QCM sensors are very interesting for practical applications owing to their high sensitivity and ease of measurement. QCM measurements rely on the Sauerbrey equation, which relates the change in the resonant frequency of a quartz crystal ( $\Delta f$ ) to the change in mass due to gas adsorption on the crystal ( $\Delta m$ ):

$$\Delta f = \frac{2f_o^2}{A\sqrt{\rho_q\mu_q}} \Delta m$$

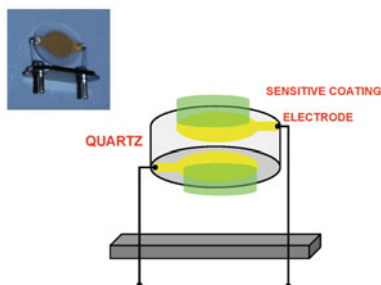
where  $f_o$  is the resonant frequency of the unloaded crystal,  $A$  is the active area of the crystal between the two electrodes,  $\rho_q$  is the density of the quartz ( $2.648 \text{ g/cm}^3$ ), and  $\mu_q$  is the shear modulus of quartz ( $2.947 \times 10^{11} \text{ g/(cm s}^2\text{)}$ ). The frequency shift of a QCM sensor is strongly depending on squared frequency, typically ranging from 5 to 30 MHz, and surface density ( $\Delta m/A$ ) of the sensitive film. In fact, the mass sensitivity of a QCM resonating at 10 MHz is typically in the range of  $0.1\text{--}1.0 \text{ Hz/(ng/cm}^2\text{)}$ , which is very high to detect very-low concentrations of gases up to sub-ppm level. Therefore, QCM sensitivity can be improved by mass amplification using very adsorbent materials which increase the adsorbed mass. In this context, nanomaterials with high surface area and high chemical reactivity are very useful for fabricating high-sensitivity chemical sensors with room-temperature operations for low power consumption.

Gas sensors based on carbon nanotubes (CNTs) have been studied both in the form of nanocomposites [3–7] and networked films [8, 9] for high-sensitive VOCs detection SAW and QCM applications, at room temperature. Here, CNTs multilayered films have been prepared by Langmuir–Blodgett (LB) technique onto double-side AT-cut quartz 10 MHz QCM equipped by Al electrodes. A buffer layer of Cadmium Arachidate (CdA) has been used to promote the adhesion of the CNTs multilayer onto QCM surface. The detection of volatile organic compounds (VOCs) of ethylacetate, acetone and m-xylene at enhanced mass sensitivity by QCM-sensors coated with CNTs-multilayers has been investigated by achieving linearity in the response and low limit of detection of a few ppm for a given targeted analyte.

## 42.2 Experimental Details

CNTs films were grown by CVD technology. The CNTs films were deposited onto large-size cost-effective alumina (40 mm width  $\times$  40 mm length  $\times$  0.6 mm thickness), coated with growth-catalyst of iron (Fe) nanoclusters with a nominal thickness of 2.5 nm and sputtered at  $10^{-2}$  Torr. The Fe-catalysed alumina

**Fig. 42.1** Scheme of the QCM-sensor measured and image of a typical QCM



substrates were heated to 750°C by a rate of 10°C/min in H<sub>2</sub> atmosphere upon flow of 100 sccm at a total pressure of 1.5 Torr. In the gas-plasma, the flow rate ratio between C<sub>2</sub>H<sub>2</sub> and H<sub>2</sub> was kept constant at 20/80 sccm, respectively. The CNTs deposition was performed at a constant pressure and temperature of 5 Torr and 750°C, respectively for 30 min by depositing a vertically-aligned CNTs film with thickness of 10–12 μm.

After CNTs growth, the nanomaterial was mechanically removed from substrate to prepare a solution as precursors for the LB film deposition. A dispersion of the CNTs in a DMF solvent has been prepared to promote their de-bundling before LB film deposition. In addition, a buffer layer of cadmium arachidate (CdA) has been used to promote the adhesion of the CNTs multilayer onto QCM surface.

The scheme of the QCM sensor is shown in Fig. 42.1. A piezoelectric sensor based on unloaded AT-cut quartz oscillating at a frequency of 10 MHz has been used as transducer equipped by Al electrodes with an active area of 12.56 mm<sup>2</sup>.

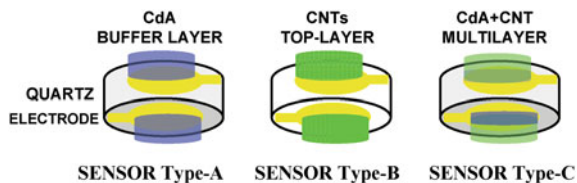
Three different QCM-sensors have been fabricated by depositing LB layered films as depicted in the Fig. 42.2. The process parameters for LB film deposition are reported elsewhere [3–6, 8]. The QCM sensors investigated are so-described:

*Sensor type-A*—10 MHz AT-cut quartz QCM coated by a LB film of CdA with a thickness of 10 layers onto double-side of the quartz.

*Sensor type-B*—10 MHz AT-cut quartz QCM coated by a LB film of CNTs with a thickness of 10 layers onto double-side of the quartz.

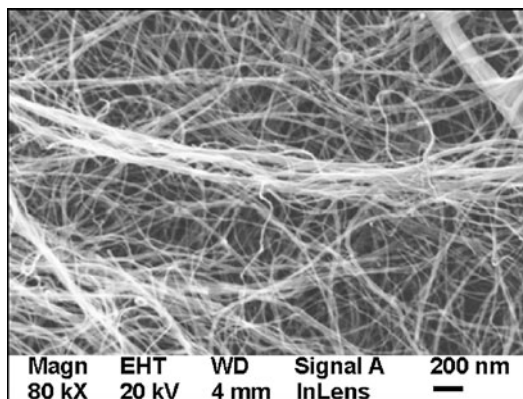
*Sensor type-C*—10 MHz AT-cut quartz QCM coated by a LB multilayered film of CNTs with a thickness of 10 layers onto the buffer layer of CdA with a thickness of 10 layers onto double-side of the quartz.

The so-fabricated QCM sensors have been located in a test cell (1500 ml volume) for gas exposure measurements. The cell case is able to host up to twelve piezoelectric sensors. Dry air was used as reference gas and diluting gas to air-conditioning the sensors. The gas flow rate was controlled by mass flowmeters. The total flow rate per exposure was kept constant at 1500 ml/min. The gas sensing experiments have been performed by measuring the resonant frequency of the three QCM sensors upon controlled ambient of individual volatile organic compounds (VOCs) of ethylacetate, acetone and m-xylene in the range of 160–495, 265–800, and 16–50 ppm, respectively, at sensor temperature of 20°C.



**Fig. 42.2** Three different types of investigated QCM-sensors coated at double-side by **a** CdA buffer layer; **b** CNTs top-layer film and **c** CNT multilayer onto CdA buffer layer

**Fig. 42.3** FE-SEM image of CNTs treated with DMF and prepared on Si substrate



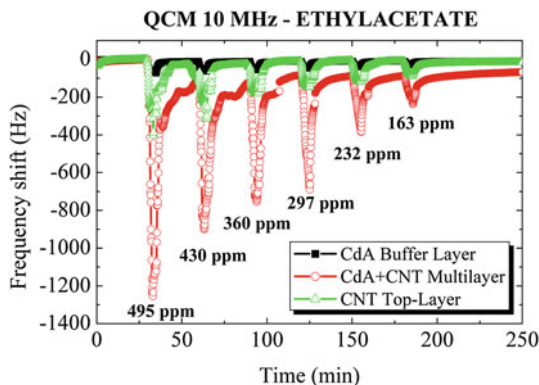
The frequency output of the QCM-sensors has been measured by a frequency counter (Agilent, 53132A) with a multiplexed read-out by a switch unit (Agilent, 34970A) driving two 50  $\Omega$ , 4  $\times$  1 rf multiplexers (Agilent, 34905A). A J-type thermocouple was used to control the temperature in the sensor cell and its voltage output was measured by a multimeter (Agilent, 34401A). Data were collected and stored for further analysis in a PC interfaced with a GPIB card in the VEE-software ambient (Agilent).

### 42.3 Results and Discussion

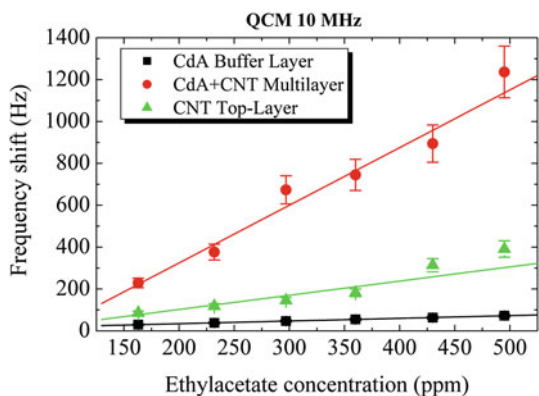
The morphology and structure of the CNTs multilayer, treated with DMF solvent, has been characterized by FE-SEM, as reported in Fig. 42.3. A substrate of silicon has been used to deposit DMF-treated CNTs layers for electron microscopy observations. A dense network of bundles of multiple tubes consisting of multi-walled carbon nanostructures appears with a maximum length of 5  $\mu\text{m}$  and single-tube diameter varying in the range of 5–35 nm.

Figure 42.4 shows the typical time responses in terms of frequency shift for three QCM sensors based on LB films of CdA buffer layer, CNTs top-layer, and multilayer of CNTs films onto buffer CdA, exposed towards 5 min six pulses of

**Fig. 42.4** Room-temperature time response towards 5 min six pulses of ethylacetate for three QCM sensors coated by CdA buffer layer, or CNT layer, or CdA + CNT multilayer



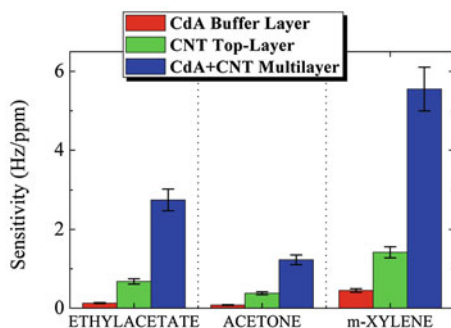
**Fig. 42.5** Calibration curves of the three 10 MHz QCM-sensors to ethylacetate, at room temperature



ethylacetate, at room-temperature. The resonant frequency of all CNTs-sensors decreases upon a single exposure of the ethylacetate caused by the mass loading of the molecules adsorption. All three QCM-sensors demonstrate reversibility of the response upon switching of the target analyte concentration into dry air. In addition, a total recovery of the baseline frequency for all QCM-sensors has been measured. The highest mass sensitivity has been achieved for multilayer CdA + CNTs due to the greatest gas adsorbed mass. A linearity in the calibration curves for all QCM-sensors was measured, as reported in Fig. 42.5.

The gas sensitivity, expressed by the slope of the linear curves, has been plotted towards three tested different analytes (ethylacetate, acetone, m-xylene) for all three studied coatings, as reported in Fig. 42.6. These results demonstrate that multilayer CdA + CNTs exhibits the maximum sensitivity measured for three VOCs under test due to its highest capability of gas adsorption. A decreasing sensitivity towards aromatics (m-xylene), esters (ethylacetate) and ketones (acetone) has been detected for any considered sensitive coating.

The gas adsorption can be considered as the contribution of the main sensing mechanism of mass loading, as measured by the linearity in the gas response in terms of frequency shift as a function of gas concentration.



**Fig. 42.6** Room-temperature pattern sensitivities of the three 10 MHz QCM-sensors coated by CdA buffer layer, or CNT layer, or CdA + CNT multilayer towards three different VOCs of ethylacetate, acetone and m-xylene. The range of the tested gas concentration of ethylacetate, acetone and m-xylene is 163–495, 265–800, and 16–50 ppm, respectively

## 42.4 Conclusions

CNTs-multilayer for 10 MHz QCM sensors have been prepared by Langmuir-Blodgett technique for enhanced mass sensitivity to detect VOCs of ethylacetate, acetone, and m-xylene up to ppm level of concentration, at room temperature. Chemical sub-ppm level of the VOCs is potentially measurable by tested QCM-sensors. The sensing properties have been investigated comparing the gas response of the buffered and un-buffered CNT multilayers to maximize sensitivity of the CNT sensors. The results demonstrate that the CdA-buffered CNTs-multilayer exhibits the highest gas sensitivity towards tested VOCs of ethylacetate, acetone and m-xylene, at room temperature. This is caused by the mass loading of the adsorbed gas molecules.

The CNTs-multilayers based QCM-sensors show high sensitivity, linearity, fast response, potential sub-ppm detection level, good reproducibility and reversibility. The studied QCM sensors with enhanced gas sensitivity and broader selectivity based on CNTs-multilayers are useful for chemical detection at room temperature and low power consumption and for applications in environmental air-emission monitoring.

## References

1. Ballantine DS, White RM, Martin SJ, Ricco AJ, Zellers ET, Frye GC, Wohltjen H (1997) Acoustic wave sensors. Academic Press, San Diego
2. Rabe J, Buttgenbach S, Schroder J, Hauptmann P (2003) Monolithic miniaturized quartz microbalance array and its application to chemical sensor systems for liquids. *IEEE Sens J* 3(4):361–368
3. Penza M, Tagliente MA, Aversa P, Cassano G, Capodiceci L (2006) Single-walled carbon nanotubes nanocomposite microacoustic organic vapor sensors. *Mater Sci Eng C* 26:1165–1170

4. Penza M, Tagliente MA, Aversa P, Cassano G (2005) Organic vapor detection using carbon nanotube composites microacoustic sensors. *Chem Phys Lett* 409:349–354
5. Penza M, Tagliente MA, Aversa P, Re M, Cassano G (2007) The effect of purification of single-walled carbon nanotube bundles on the alcohol sensitivity of nanocomposite Langmuir-Blodgett films for SAW sensing applications. *Nanotechnology* 18:185502
6. Penza M, Aversa P, Cassano G, Wlodarski W, Kalantar-zadeh K (2007) Layered SAW gas sensor with single-walled carbon nanotube based nanocomposite coating. *Sensor Actuat B* 127:168–178
7. Chen H-W, Wu R-J, Chan K-H, Sun Y-L, Su P-G (2005) The application of CNT/nafion composite material humidity sensing measurement. *Sensor Actuat B* 104:80–84
8. Consales M, Campopiano S, Cutolo A, Penza M, Aversa P, Cassano G, Giordano M, Cusano A (2006) Sensing properties of buffered and not buffered carbon nanotubes by fiber optic and acoustic sensors. *Meas Sci Technol* 17:1220–1228
9. Su P-G, Tsai J-F (2009) Low-humidity sensing properties of carbon nanotubes measured by a quartz crystal microbalance. *Sensor Actuat B* 135:506–511