

Polymer coated quartz crystal microbalance sensors for the detection of volatile organic compounds

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Abstract

In this work, plasma polymerization of tetraethoxysilane (TEOS) has been used for producing QCM chemical sensors. The sensor was exposed towards the methanol and chloroform molecules. The measured isotherms on modified QCM electrode showed a good reproducibility and reversibility. Generally, the frequency shift (Δf) of QCM increases linearly with the vapor concentration. The evolution of sensor response showed clearly an improvement of the QCM sensibility. However, the film elaborated from 50% of TEOS and 50% of O_2 was found to be significantly more sensitive than film deposited from high proportion of oxygen due to dense structure. Concerning the selectivity, the results revealed a good affinity of the layer to methanol molecules. Fourier transform infrared spectroscopy (FTIR) analysis showed that VOCs molecules interact via hydrogen bonding due to the presence of the $-OH$ group in the elaborated layers.

Keywords: Quartz crystal microbalance; TEOS film; Volatile organic compounds; sensor

1. Introduction

The detection of volatile organic compounds (VOCs) in environmental protection, health care and industrial processing has been a subject for research and development over the last decades. Alcohols such as methanol and ethanol are used in many workplaces and laboratories, medicine and food industry [1]. The development of sensors with selectivity, rapidly, reliability and reproducibility to VOCs becomes more interest. A number of electronic devices and chemical sensors based on the use of different polymer coatings such as, mass sensitive quartz crystal microbalance (QCM) and surface acoustic wave (SAW) devices have been developed. Amongst the various types of chemical sensors, there is a considerable interest in QCM [2-3] for detection of VOCs. Quartz crystal microbalance (QCM) sensors coated with various sensing films have been useful for gas/vapor detection and analysis [4]. Polymers are widely used as chemically sensitive coating materials on quartz crystal electrodes and are particularly suitable for detecting VOCs, because of the ability of the polymer to sorb vapour reversibly. The chemical structure and physical properties of polymeric coatings and the nature of interaction between polymer coatings and vapour molecules determine the selectivity, sensitivity, signal kinetics and reversibility of the sensors [5]. QCM is extremely sensitive to mass change. The surface of a quartz crystal electrode is coated with a sensitive polymeric material, capable of interacting with the environment of interest and able to adsorb vapour reversibly [6]. The changes in mass (m') of

the polymer film can be measured by the oscillating frequency of the quartz electrode. The frequency change (Δf) to the mass loaded is calculated from Sauerbrey equation [7]:

$$\Delta f = - \left(\frac{2f_0^2}{\sqrt{\rho_Q \mu_Q}} \right) m'$$

Where f_0 (Hz) is the natural frequency of the quartz crystal, ρ_Q is the quartz density (2.649 g cm⁻³) and μ_Q is the shear modulus (2.947×10¹⁰ N/m²). In this work, a simple coating method has been used for producing QCM chemical sensors. The method is based on plasma polymerization of TEOS (PTEOS). The sensor was exposed towards a wide range of VOCs molecules (polar and non polar), such as methanol and chloroform. The paper presents results on the effect of some discharge parameters on sorptive properties of the coated QCM. We investigated the correlation between the interaction of the analyte with the sensitive layer and the chemical structures of the elaborated layers by means of Fourier transform infrared spectroscopy (FTIR) analysis.

2. Experimental

2.1. Chemical products and instrumentation

Tetraethylorthosilicate (TEOS) was purchased from Merck and used without further purification. The response of the sensor was tested using methanol and chloroform as the analyte species. Six megahertz, AT-cut QCM with polished gold electrodes (diameter 5 cm) were purchased from International crystal Manufacturer (ICM). The frequency change of the sensor (adsorption measurements) was monitored by QCM measurement equipment.

2.2. Polymeric film production

TEOS thin films were deposited using plasma enhanced chemical vapor deposition (PECVD) at low frequency power from pure vapor of TEOS or diluted with oxygen. The power during the polymerization was controlled by a 19 kHz generator. The system consisted of a bell-jar chamber (310 mm diameter, 450 mm high), a pair of parallel symmetrical electrodes (120 mm diameter) separated by a distance of 2.5 cm, vacuum system (composed of Alcatel primary pump) and a monomer inlet system. The pressure in the reactor was monitored by a pressure measurement system (Pirani). Substrates were placed in the grounded lower electrode and the reactor chamber was pumped down to 1 Pa in few minutes. The plasma polymerized films were deposited simultaneously on QCM and on intrinsic silicon wafers for FTIR analysis. Chemical structure and composition of PPTEOS films were characterized by FTIR spectroscopy. All spectra were acquired in absorbance mode in the 400-4000 cm^{-1} range using a Nicolet Avatar 360 FTIR spectrometer. The film thickness was measured using a Tencor profilometer.

2.3. Measurement systems of the QCM gas sensors

The experimental set-up is shown in Fig. 1. Organic vapor was generated by continuously heating the solution and are introduced to the testing cell by pressure difference. An automatic mass flow controller monitored the target analyte gas concentrations that were fed to the chamber and upon attaining the desired concentration, the shift frequency was simultaneously recorded and the data were transferred to a computer via RS232 interface. Between measurements, the chamber was evacuated to desorb analyte.

3. Results and discussion

3.1. Reproducibility and reversibility of the sensor

To investigate the reproducibility of the sensor, the response signals of QCM sensors coated with 693 nm layers thickness, deposited from pure TEOS exposed to methanol and chloroform vapors at concentration of 300 ppm were recorded. The sensor was repeated for three times to insure a good reversibility and reversibility Fig.2. After reaching steady state, the film was exposed to dry air until full desorption of the crystal was obtained and it was then exposed to previously used analyte concentration. Moreover, the sensor is found to be reasonably selective and significantly sensitive to methanol vapor than the chloroform vapor.

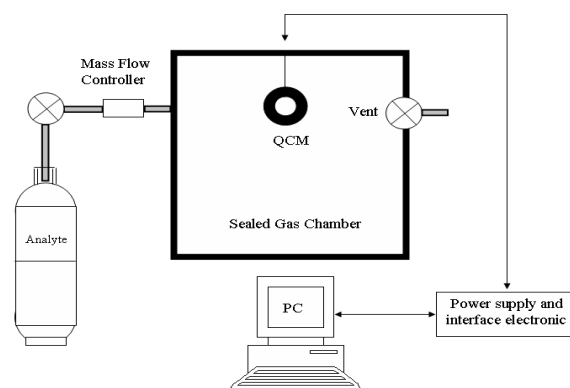


Figure 1. A schematic diagram of QCM experimental cell.

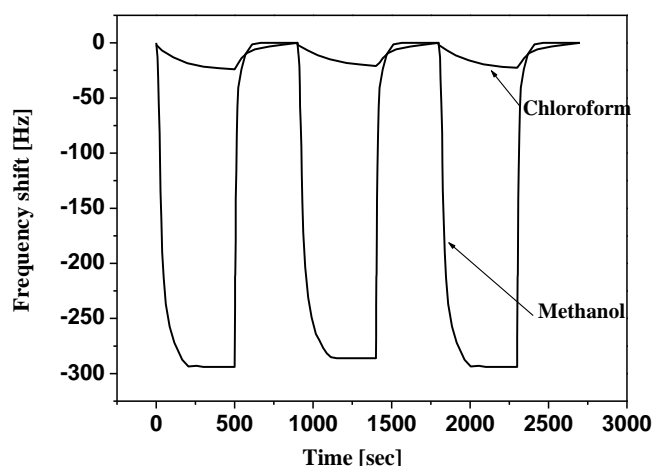


Figure 2. Reproducibility and reversibility of coated QCM electrode when exposed to organic vapors

3.2. Coating the electrode of QCM with TEOS/O₂ film for organic vapor sensing

During films deposition, the partial pressure of TEOS/O₂ and discharge power were kept constant equal to 0.4 mbar and 8 W, respectively. The proportion of oxygen in the mixture was varied from 0 % to 80 %. The QCM sensors coated with 693 nm layers thickness was exposed to methanol and chloroform vapors with various concentrations. Fig. 3 presents the plots of shift frequency (Δf) as a function of analyte concentration for different oxygen proportion in the mixture. We observe over the whole explored domain of concentrations a good linearity of the sensors responses for both virgin and coated quartz. Moreover, it clearly noticed that the use of a thin PPTEOS film deposited on quartz crystal improves considerably the sensibility of the sensor. For a concentration of methanol of about 250 ppm, the shift frequency recorded on virgin quartz is in the order of 5 Hz. This later value passes to about 250 Hz when the QCM electrode is functionalized with pure TEOS film. This improvement of the sensitivity can be explained either by an increase of the surface adsorption sites of the coated electrode and/or by the physico-chemical

properties of the elaborated layer. This variation of the sensitivity of the QCM with increasing target concentration suggests the existence of a diffusion process of the organic molecules into the bulk of the coating and the increase in film thickness would encourage at first the multiplication of the absorption sites resulting in increased sensitivity of the QCM [8]. For film elaborated from 50% of oxygen and 50% of TEOS, the shift frequency increases significantly to reach a value of about 900 Hz when the sensor was exposed towards 250 ppm. The sensibility improvement of the coated QCM exceeds 180 times the sensibility recorded on virgin quartz crystal. However, we notice that beyond a certain proportion of oxygen in the mixture, the sensitivity decreases significantly. For films elaborated with 80 % of oxygen in the mixture, the response towards 250 ppm of methanol vapors falls to reach 160 Hz, but remained still higher than recorded on virgin quartz crystal. The deposited films became inorganic in character with SiO₂ as type chemical composition closer to thermal silica (vitreous, more rigid, are less permeable).

In fig 3b, we notice that the sensitivity to chloroform molecules is much lower than that recorded for the methanol molecules: for 250 ppm of chloroform, the frequency shift is only 20 Hz for quartz coated with pure TEOS film and hardly exceeds 43 Hz when the film

elaborated from 50% of oxygen and 50% of TEOS. This difference in sensitivity of quartz covered with the same film thickness and same proportion of oxygen in the mixture can be explained by the difference in the molar weight between methanol and chloroform: The molecules of chloroform having a molar weight much more important than that of methanol molecules which have much difficulty to pass through the pores existing in the thin films.

The infrared spectra obtained for different percentages of oxygen in the mixture TEOS/O₂ are shown in Fig.4. We notice that for strong proportions of oxygen (80%) the recorded infrared spectrum becomes close to that of thermal silica with its three principal peaks attributed to SiOSi binding group around 400, 800 and 1070 cm⁻¹ [9]. Indeed, we observe a total disappearance of the peaks assigned to the element carbon. For film deposited with 50% of oxygen, the CH_x group (2962 cm⁻¹) appears with low and we observe a total disappearance of the SiH group (2250 cm⁻¹). Table 1 shows the variation of peak intensities ratio of CH_x and SiOH relative to SiOSi peak. With 50% of oxygen, the small decrease of CH_x peak is compensated by an increase of hydroxyl groups. A low dense film structure with high proportion of hydroxyl groups promote gas sorption, which is consistent with large sorption capacity of the film elaborated with 50% of O₂.

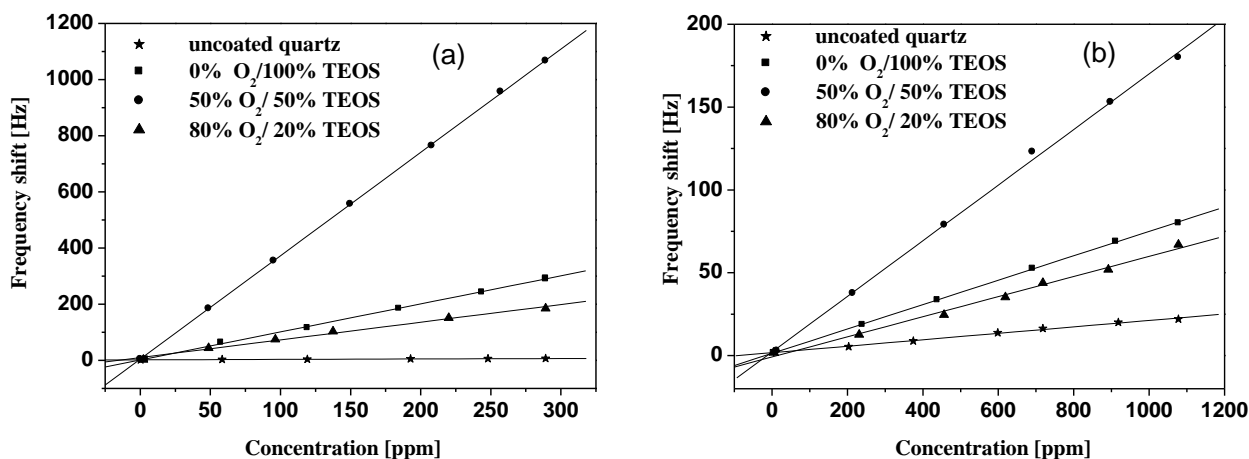


Figure 3. Variation of shift frequency with the concentration of: (a) methanol and (b) chloroform for different oxygen proportion

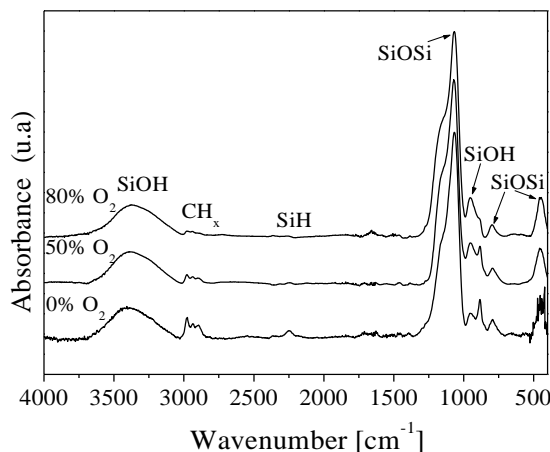


Figure 4. FTIR spectra of the deposited layers elaborated from a mixture of TEOS and oxygen

Proportion of oxygen [%]	Peak ratio SiOH / SiOSi	Peak ratio CH _n /SiOSi
0	0.13043	0.08261
50	0.15092	0.03736
80	0.14384	0.01712

Table.1 Variation of the SiOH and CH_n relative peak intensity as a function oxygen proportion in the mixture.

4. Conclusion

In case of coated QCM electrode with a sensitive layer elaborated from pure vapor of TEOS, the evolution of sensor response showed clearly an improvement of the sensor sensibility for both types of analyte. The frequency shifts versus analytes concentrations exhibited satisfactory linear relationship. The results showed that smaller molar weight VOC molecules are more absorbed than greater molar weight VOC molecules indicating a strong affinity of PTEOS film for methanol gas. Film elaborated from 50% of TEOS and 50% of O₂ was found to be significantly more sensitive than film deposited from high proportion of oxygen due to dense structure. FTIR analysis suggests that the presence of CH_n groups in the film structure (which increases the film microvoides) and OH groups (which provide a main source for hydrophylic capability to interact with foreign molecules) increase the gas sorption capacity of the elaborated layer.

References

- [1] G. Ziem, J. Metamney, *Environmental Health Perspectives* 105 (1997) 417.
- [2] G.J. Price, A.A. Clifton, V.J. Burton, T.C. Hunter, "Piezoelectric chemical sensors based on morpholine containing polymers", *Sens. Actuators B: Chem.* 84 (2002) 208.
- [3] N.E. Agbor, M.C. Petty, A.P. Monkman, "Polyaniline thin films for gas sensing", *Sens. Actuators B* 28 (1995) 173.
- [4] Bartosz Wyszynski, Agustin Gutierrez Galvez, Takamichi Nakamoto, "Improvement of ultrasonic atomizer method for deposition of gas-sensing film on QCM", *Sens. Actuators B* 127 (2007) 253-259
- [5] Mohamad M. Ayad, Gad El-Hefnawey, Nagy L. Torad, "Quartz crystal microbalance sensor coated with polyaniline emeraldine base for determination of chlorinated aliphatic hydrocarbons", *Sens. Actuators B: Chem.* 134 (2008) 887-894
- [6] G.G.Wallace, G.M. Spinks, L.A.P. Kane-Maguire, P.R. Teasdale, "Conductive Electroactive Polymers: Intelligent Materials Systems", second ed., CRC Press, Boca Raton, 2003.
- [7] G. Sauerbrey, "The use of quartz oscillators for weighing thin layers and for microweighing", *Z. Phys.* 155 (1959) 206.
- [8] Jennifer UBRIG, "Encapsulation de dispositifs sensibles a l'atmosphère par des dépôts couches minces élaborés par PECVD", Doctorat thesis, Polytechnic school, 28 November 2007,
- [9] K. Kim, D. Kwon, G. S. Lee, "properties of low dielectric constant fluorinated silicon oxide films prepared by plasma enhanced chemical vapor deposition ", *Thin Solid Films* 332 (1998) 369-374.