VOC sensing properties of plasma coated QCM based sensor related to monomer flow rate

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Abstract: Hexamethyldisiloxane (HMDSO) thin films coated quartz crystal microbalance (QCM) electrodes have been characterized for the detection of volatile organic compounds (VOCs). The sensitive coatings were plasma polymerized in pure vapor of HMDSO with different monomer flow rate. The sensor sensitivity was evaluated by monitoring the frequency shift (Δf) of the coated QCM electrode exposed to different concentrations of benzene, chloroform and their mixture. Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Force Microscopy (AFM) were used to study the chemical composition and surface morphology of the plasma polymerized sensitive layers. The results show that surface roughness combined with chemical structure significantly affects the sensitivity of the QCM-based sensor.

Keywords: monomers, PECVD, Volatile organic compounds, AFM, FTIR

1. Introduction

Volatile organic compounds (VOCs) are found in ambient air due to human activities and natural sources. The identification and monitoring of VOCs have become serious tasks in many countries of the world and are important for the early control of environmental pollution [1]. The analysis of gases represents one of the main objectives of current research in the sensor field [2, 3]. Due to their low price, fast response and ready integration into electronic circuits, one widely investigated device is the Quartz Crystal Microbalance (QCM) [4]. In order to be used as chemical sensor, the QCM electrode is coated with sensitive layer capable of interacting with the chemical species of interest. At present, a great variety of sensitive polymers materials have been successfully employed as coating of QCM sensors especially for monitoring environmental pollutants [5, 6]. There is an interest in using plasma polymerized films as sensitive layers in chemical sensors because they can be deposited on any substrate and feature excellent mechanical and thermal stability and have low fabrication cost [7, 8].

In this study, plasma polymer materials were deposited in low frequency plasma reactor from pure vapor of HMDSO on QCM gold electrode substrates. Among the numerous parameters, which have an influence on the synthesized plasma film structure, the monomer flow rate is fundamental. In fact, this parameter could be related to the monomer fragmentation degree and radicals concentration in the plasma reactor. During polymerization the partial pressure of HMDSO has been varied in order to elaborate VOC sensor with different sensing properties. The sensor response in terms of QCM frequency shift was evaluated towards different concentration of chloroform, benzene and their mixture. The structural analysis of the elaborated sensitive layers was carried out by Fourier transform infrared (FTIR) spectroscopy and the morphological properties were investigated by Atomic Force Microscopy (AFM).

2. Experimental

Thin sensitive layers were elaborated using plasma Enhanced chemical vapor deposition (PECVD) technique [9]. The films were deposited in low frequency plasma reactor from pure vapor of HMDSO at different monomer flow rate. The power during polymerization was controlled by a 19 kHz generator. The system consisted of parallel symmetrical electrodes, 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). Samples were placed in the grounded lower electrode and the reactor chamber was pumped down to 10 Pa. A partial monomer pressure was adjusted to 15, 30, 40 and 50 Pa to investigate their effects on the sensing properties of the elaborated sensor. The evaluation of sensors responses were carried out by monitoring the frequency shifts of the quartz exposed to two various VOCs vapors and their mixture. The experimental setup is illustrated in Fig.1. In the step of individual detection, a liquid of known volume and density was introduced in the testing cell and heated to evaporate freely. After evaporation and diffusion towards the electrode surface, the injected vapor was...
subsequently adsorbed onto the functionalized QCM electrode surface, which induced a frequency shifts.

Fig. 1. Sensor response characterization of individual and binary gas mixture.

The sensitivity of the elaborated QCM sensors was evaluated towards different concentrations varied from about 40 to 200 ppm. In the step of gas mixture detection, the individual VOCs (benzene and chloroform) were introduced separately at the same time in the testing cell and heat together to evaporate. The values of $\Delta f$ were transferred to a computer via RS232 interface.

Chemical structure and composition of the deposited 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.

Surface morphology of the QCM coating was studied using the Agilent Technologies 5420 Scanning Probe Microscope. The surface roughness was examined on a nanometer scale and AFM images were recorded in contact mode with scan area of 5 µm × 5 µm.

3. Results and discussion

Fig. 2 shows the relation between concentration and shift frequency of QCM coated from HMDSO at different pressure. It is clearly seen that $\Delta f$ versus analyte concentrations exhibited satisfactory linear relationship. The sensitive layer was found to be reasonably selective and more sensitive to chloroform vapor than benzene vapors. The sensor coated from HMDSO at 40 Pa presents a great sensitivity to VOC than other monomer layers.

![Graphs showing variation in shift frequency of QCM coated by HMDSO at different pressures](image)

Fig. 2. Variation in shift frequency of QCM coated by HMDSO at: (a) 5 Pa, (b) 20 Pa, (c) 30 Pa and (d) 40 Pa as a function of the concentration of chloroform and benzene.

Fig. 3 showed the differential frequency shifts of the four QCM sensors exposed to four different concentrations of binary mixture of chloroform and benzene. It can be seen from the bar chart (Fig. 3) that there is significant statistical variation between the frequency response curves of the sensors.

FTIR spectra of the HMDSO films deposited at various pressures are shown in Fig. 4. When plasma polymerization is performed in pure vapour of HMDSO, IR spectra exhibit a main absorbance in the
2960 - 2850 cm\(^{-1}\) range related to CH\(_x\) groups. It clearly seen that increasing the HMDSO flow rate, there is an increase of hydrocarbons (CH\(_x\)), methyl groups Si-(CH\(_3\))\(_3\) and Si-H with the decrease of hydroxyl groups. The increase of methyl groups makes the film more hydrophobic. It would be expected that QCM sensor coated with hydrophobic film can detect volatile organic compounds with decreasing water effect from ambient conditions because of hydrophobicity. These behaviors justify the high sensitivity observed for QCM sensor coated at high pressure of HMDSO.

Fig. 3. Frequency response of QCM for a binary mixture of chloroform and benzene at different concentration.

Fig. 4. FTIR spectra of plasma-polymerized coating of HMDSO at: (a) 5 Pa, (b) 20 Pa, (c) 30 Pa and (d) 40 Pa.

Fig. 5 depicts a typical high resolution AFM images. The elaborated sensitive coatings are continuous and pinhole-free with no cracks.

Fig. 5. AFM characterization of the QCM sensor surface coated at: (a) 5 Pa, (b) 20Pa, (c) 30 Pa and (d) 40 Pa.
Nanoparticles with varying sizes and quantities were seen to be randomly distributed throughout the surface of the deposited film. The aggregates dimensions were in the range of about 50 - 300 nm. The surface roughness increases from 6.97 nm to about 20 nm with increasing HMDSO partial pressure. The increase in surface roughness leads to the increase in the specific surface area due to large surface to volume ratio. The enhanced sensor surface area can then accommodate more adsorption sites, which justifies the enhanced adsorptive properties of QCM sensor coated from HMDSO film deposited at monomer flow rate of about 40 Pa.

4. Conclusion

As demonstrated by FTIR and AFM analyses, the chemical structure and surface morphology of the coated QCM sensors are clearly correlated with their sensing properties. The QCM sensor coated with hydrophobic film would be sensitive to VOCs molecules due to the interaction with methyl groups on the sensitive coating surface. AFM images revealed the increase of the surface roughness, leading to the increase of the sensor sensitivity. Surface morphology combined with the chemical composition strongly affects the sensitivity of the coated QCM sensor.

5. References