Hexamethyldisiloxane thin films as sensitive coating for quartz crystal microbalance based volatile organic compounds sensors

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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 and HMDSO/O_2 mixture. The sensor sensitivity was evaluated by monitoring the frequency shift (Δf) of the coated QCM electrode exposed to different concentrations of VOC vapors, such as ethanol, methanol, benzene and chloroform. The isotherm response characteristics showed good reproducibility and reversibility. For all types of analyte, Δf were found to be linearly correlated with the concentration of VOC vapor. It was shown that it is possible to tune the chemical affinity of the sensor by changing the oxygen ratio in the deposition gas mixture. Contact angle measurements (CA), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to study surface wettability, chemical composition and surface morphology of the coated QCM electrodes. ATR-FTIR analysis showed the presence of methyl groups around 840 cm^{-1} due to Si–$(CH_3)_3$ rocking vibration making the elaborated sensor surface hydrophobic. When the coating is performed in HMDSO/O_2 mixture, AFM and SEM images showed an increase in the effective specific surface area of the sensor due to the increase in surface roughness. Surface morphology combined with chemical composition significantly affects the sensitivity of the QCM-based sensor.

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1. Introduction

Volatile organic compounds (VOCs) are found in ambient air due to human activities and natural sources. High concentration exposure to some VOCs over a short or long term may cause diseases or serious irreversible effect [1,2]. VOCs do not only harm the human and survival health but also pollute the environment due to their contribution to stratospheric ozone depletion, tropospheric photochemical ozone formation and enhancement of the global green house effect [3]. 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. The analysis of gases represents one of the main objectives of current research in the sensor field. In this context, one widely investigated device is the quartz crystal microbalance (QCM), in which an increase of mass into the crystal electrode due to sorption of the analyte molecules can generate a shift of the resonance frequency (Δf) according to the well known Sauerbrey equation [4].

$$\Delta f = -C_f \Delta m. \tag{1}$$

Where, Δf is the observed frequency change, Δm is the change in mass per unit area and C_f is the sensitivity factor for the used crystal. It is generally accepted that when the mass loading from the deposit causes a change in frequency of less than 2% of the unloaded crystal frequency, Sauerbrey's equation can be used to obtain accurate results. As the thickness of the film increases, the Sauerbrey equation must be extended to incorporate the elasticity properties of the deposited films [5]. QCM sensors can measure an extremely small change on the nanogram scale and are most often investigated for online VOC detection [6–8]. These sensors are relatively simple to operate and produced a quasi-digital frequency signal with good noise and interference rejection and low rates of signal drift. Although QCM device has proved to be versatile in various application, one major disadvantage of the QCM based sensor is the limited sensitivity associated with the flat electrode surface that limits the immobilization degree of the receptor molecule per unit area. The enhancement of surface area can then accommodate more reception sites and subsequently more target analytes which enhance the sensor response. In addition to the electrode surface morphology, chemical properties of the coating materials also played an important role in the performance and affinity of the QCM sensor to a specific vapor molecule. For this purpose, the surface of the QCM electrode is coated with sensitive material capable of interacting with the chemical species of interest. The elaboration of sensitive coating is a critical task in

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design and performance of chemical sensor. At present, a great variety of sensitive polymers materials have been employed as coating of QCM sensors especially for monitoring environmental pollutants [9]. Different technologies for the synthesis of these specialized materials have included methods based on sol–gel [10], spin coating [11] and electrochemical deposition [12], but there is very few work reported in the literature, investigating VOCs sensing properties of films deposited by plasma enhanced chemical vapor deposition technique. 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 as well as insolubility in organic solvents [13]. As in case of classical polymers, the vapor sensing performances of plasma polymers are strongly related to their chemical and physical properties [14]. Their chemical and physical structures depend directly on the precursor nature and on the plasma polymerization process conditions, including discharge powers and monomer flow rate [15,16]. Porous films can be very useful for sensor development and have been a subject of research over the last decade. As an example, nanoporous silicon oxide layers have been synthesized by plasma polymerization of hexamethyldisiloxane (HMDSO) and oxygen, resulting in porous structures that have been used for sensor development [17].

In this study, plasma polymer materials were deposited in low frequency plasma reactor from pure vapor of HMDSO and HMDSO/O_2 mixture on QCM gold electrode substrates. Among the numerous parameters, which have an influence on the synthesized plasma film structure, the ratio of HMDSO/O_2 is fundamental. In fact, this parameter could be related to the monomer fragmentation degree and radical concentration in the plasma reactor [18]. The gas sensing properties of the coated QCM electrodes have been evaluated towards a wide range of VOC molecules (polar and non polar), such as ethanol, methanol, benzene and chloroform. The QCM-based sensors exhibited fairly fast response, high reversibility and linear sensitivity. The structural analysis of the elaborated sensitive layers was carried out by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and the morphological properties were investigated by Atomic Force Microscopy (AFM) and scanning electron microscope (SEM). This work, which combines ATR-FTIR, AFM and SEM analysis, aims to disclose the chemical and morphological changes associated with the addition of oxygen with the precursor. The HMDSO plasma coating of the QCM electrode used as VOC sensor aims to create hydrophobic surface for improved adsorption/desorption of VOC molecules and to grow rough surface for increased specific surface area.

2. Experimental

2.1. Reagents and apparatus

HMDSO purchased from Merck was used as precursor for the deposition of thin plasma polymerized layers. The response of the coated QCM-based sensor was tested using ethanol, methanol, benzene and chloroform as the analyte species. The frequency changes of the vibrating crystal were measured by a universal frequency counter QCM2000 (USA) connected to a personal computer via RS32 interface. The piezoelectric crystals employed in this study were AT-cut quartz crystals (USA) with the fundamental frequency of 5 MHz and 8 mm diameter circular gold electrodes on either side. All crystals were cleaned with acetone then rinsed with distilled water prior to use.

2.2. QCM coating

Thin sensitive layers were deposited using plasma enhanced chemical vapor deposition at low frequency power from pure vapor of HMDSO and mixture of 50% of HMDSO and 50% of oxygen. The use of low frequency has the advantage of high film bombardment during its growth. This bombardment favors crosslinking, improves chemical

resistance and inhibits reagents permeation, thus favoring adsorption [19]. 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. A constant partial pressure of HMDSO/O_2 vapor was adjusted to 40 Pa and injected to the reactor by pressure difference. In order to evaporate the liquid monomer and to avoid any condensation, the HMDSO flask and supply line were heated to about 50 °C. The process gas was fed from the center of the chamber through a diffusion nozzle and pumping drugs in the gas from a lower position, avoiding flow non homogeneities to an extent. The power during polymerization was controlled by a 19 kHz generator. During plasma deposition process, the resonance of the quartz decreases in accordance with the Sauerbrey equation [4]. The resonance frequency of the coated QCM was recorded in dry air and used as the absolute frequency of the sensor system.

2.3. Polymer film characterization

Contact angle measurements were performed at room temperature and atmospheric pressure. A water drop of 4 μl was released onto the coated QCM surface using a micro-syringe. The drop image was acquired by a numerical camera then transmitted to a computer for contact angle value calculation. All contact angles data were averaged from five measurements with a standard deviation of approximately 5%. ATR-FTIR spectroscopy was utilized to characterize the chemical composition of each QCM coating. Spectra were recorded using a Thermo-Nicolet avatar 360 FTIR spectrometer equipped with zinc selenide (ZnSe) multi-bounce ATR crystal, in the horizontal attenuated total reflectance mode. Spectra were acquired using a resolution of 4 cm^{-1} and a total of 32 scans. Film thickness was measured using a Tencor stylus profilometer. The QCM sensor surface roughness was examined on a nanometer scale using atomic force microscopy. AFM images were recorded in contact mode using pacific nanotechnology instruments (USA) with scan area of 0.78 μm × 0.78 μm and scan rate of 0.5 Hz/line. All scans were acquired at room temperature and atmospheric pressure and characterized by measuring the root mean square roughness (R_{rms}) and the arithmetic average of the absolute values of the surface height (R_{av}). Additionally, the surface morphology of the QCM coating was studied by SEM using Vega Tecscan microscope.

2.4. Sensor response characterization

The sensitivity of the coated QCM sensor was evaluated by monitoring the frequency shifts (Δf) of the quartz exposed to different concentrations of VOC vapors. The sensor response tests were carried out in a homemade vapor sensitivity evaluation system illustrated in Fig. 1. 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. The response of the QCM to VOC vapors was continuously monitored by a personnel computer with the aid of Labview interface software.

In this study, the resonance frequency was recorded in dry air for use as the absolute frequency of the QCM system and the frequency response was stable within ± 1 Hz over a period of several minutes. The concentration of injected analyte was calculated in part per million (ppm) according to the following equation:

$$C = \frac{\rho V_l}{V} = \frac{m_g}{V}$$