Bulgarian Chemical Communications, Volume 47, Number 4 (pp. 1039 – 1044) 2015

A superhydrophobic quartz crystal microbalance based chemical sensor for NO_2 detection

K. D. Esmeryan*, V. Georgieva, L. Vergov, J. Lazarov

Georgi Nadjakov Institute of Solid State Physics, 72, Tzarigradsko Chaussee Blvd., 1784 Sofia

Received April 23, 2015, Revised May 25, 2015

The gas sensitivity of 16 MHz carbon soot coated quartz crystal microbalances (QCMs) towards various NO_2 concentrations is investigated. The Scanning Electron Microscopy measurements reveal that the soot is deposited on the sensor surface irregularly, forming carbon nanospheres separated by nanoscale cavities. The inherent non-polar nature of the soot, along with its estimated root mean square roughness (R_{rms}) of 130 nm, transform the quartz surface into a superhydrophobic (SH) one, characterized with high static contact angle (~153 °) and low contact angle hysteresis (~1 °). Such surface configuration induces 15 Hz resonance frequency downshift of the SH QCM at low NO_2 concentrations up to 500 ppm. Furthermore, the sensor demonstrates reversible gas sorption ability in the same gas range. Further gradual increase in the NO_2 concentration up to 5000 ppm leads to an additional sensor response of 38 Hz; however, after dry air scavenging the sensor reaches its baseline with a slow rate of ~0.33 Hz/min. In addition, upon ambient humidity increase of 45 %, the SH QCM shifts down its resonance with 45 Hz, whereas the 16 MHz WO_3 coated counterpart with 212 Hz. These results clearly indicate the advantage of the soot coated QCM, which could be used for continuous *in situ* monitoring of air pollutants with negligible cross sensitivity to humidity of 1Hz/% RH.

Key words: Quartz Crystal Microbalance**,** Superhydrophobicity, Gas-sensitivity, Carbon soot.

INTRODUCTION

Nowadays, one of the major problems related with the environmental protection is the air pollution by toxic gases [1]. In particular, the nitrogen dioxide (NO_2) is an irritant gas released during fuel combustion, which at high concentrations is responsible for the formation of acid rain, ground-level ozone and enhancement of the global green house effect [2]. Therefore, over the last few years, the detection of NO_2 has been an aim of various research groups around the world [3-5]. The methods for gas analysis are based on gas chromatography, mass spectrometry, infrared spectrometry and cavity enhanced absorption spectroscopy (CEAS). Each sensing mechanism has advantages such as high sensitivity and low detection limit, and disadvantages, e.g.., requirement of grab-samples and off-site analysis, time consumption, etc. As an alternative, many researchers have focused on the use of quartz crystal microbalance (QCM) based chemical sensors due to their miniature size, low power consumption, high sensitivity and resolution, fast response-recovery time and relatively low cost [6-10]. During “real-world” monitoring of the quality of air, two external factors are of crucial importance for the accurate QCM performance, namely the ambient temperature and humidity. While the methods of temperature control are sufficiently well documented [11-13], a very few is known about the compensation of relative humidity (RH). The latter has an interfering influence on the sensor resolution and sensitivity, as the adsorbed water vapor impedes the interaction between the gas analyte and the sensitive layer [14]. Furthermore, the changes in ambient humidity induce cross sensitivity of the QCM, which cause measurement errors, similar to the temperature effect [15, 16]. Recently, the humidity compensation has been implemented by means of a dual QCM oscillator circuit [17] or computational algorithms [18]. Such techniques are accurate, but they are insufficient in regard to the reduced gas sensitivity, caused by the water vapor-occupied active adsorption sites of the sensing surface [14]. This drawback could be overcome by utilizing a superhydrophobic (SH) sensitive coating. With their extreme non-wettability, expressed through static water contact angle greater than 150° and contact angle hysteresis ≤5° [19], the superhydrophobic coatings stand out as facile solution, because they inhibit the accumulation of water vapor on solid surfaces. This phenomenon may be explained through the heterogeneous nucleation theory [20] and has been verified for QCM coated with SH

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* To whom all correspondence should be sent:
E-mail: karekin_esmerian@abv.bg

silica film [21]. Unfortunately, these experiments are inconsistent with the theory, showing higher frequency shifts of the SH QCM compared to an uncoated device. According to Sauerbrey's equation [22], this is associated with larger amount of water vapor adsorbed on the SH sensor surface.

Therefore, the primary objective of this paper is to investigate the applicability of 16 MHz superhydrophobic carbon soot coated QCMs for *in situ* detection of various NO_2 concentrations. In addition, our experiments will be used to validate the hypothesis that superhydrophobicity inhibits the accumulation of water vapor on solid surfaces. The latter is crucial if the sensor is intended to operate in "real-world" environmental conditions. Section 2, gives brief description of the fabrication process and surface characterization of the soot coatings. Furthermore, the gas sensing measurement setup is discussed. Section 3, summarizes the experimental results for the gas sorption-desorption ability of the sensitive layer. Also, the relation between the surface wettability and humidity sorption is considered in terms of the heterogeneous nucleation theory.

EXPERIMENTAL

Surface coating fabrication

The technique we used is based on the incomplete combustion of carbon nanoparticles contained in a rapeseed oil mixture [23]. Firstly, 100 ml of rapeseed oil are added to an evaporating glass dish. A gauze based wick is immersed in the oil and then ignited until a black carbon fume occurred. In this study, a few microscope glass slides and 16 MHz AT-cut QCMs were exposed over the fume, which caused deposition of carbon soot on the substrate surface. The wettability of soot coatings is investigated through static contact angle, contact angle hysteresis and roll-off angle measurements for droplets of water, by using a high speed camera Nac Memrecam HX-6. These were found to be in the range of 151-154 °, 0.2-4 ° and 2-10 °, respectively, confirming superhydrophobic surfaces with mobile droplet behavior [19].

Surface characterization

The surface morphology and roughness were examined by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The experiments were carried out using a JSMT 200 (Jeol) SEM with magnification of 50k and an AFM Multimode V (Bruker, Santa Barbara, CA). During SEM analysis, the samples were studied and imaged in secondary electron mode. The observations were preceded by a vacuum deposition of several nanometer thick films of carbon and gold. AFM imaging was performed in tapping mode and height, amplitude and phase images were recorded. At least two different points on the sample surface were explored. For all measurements, the image resolution was 512 lines per scan direction. Silicon cantilevers for soft and fragile surfaces with a cantilever length of 125 µm and Al reflective coating on the backside (HQ-NSC19-Al BS, MikroMasch) were used in the experiments. These cantilevers have a nominal resonance frequency of ca. 65 kHz and a typical force constant of 0.5 N/m. The tip nominal radius is less than 8 nm. For 1 µm scan, the used scan rate was 0.45 Hz.

Gas sensing measurement setup

The gas sensing properties of 16 MHz carbon soot coated QCMs were studied by exposure to different NO_2 concentrations. The QCMs were fabricated on AT-cut quartz plates. On both sides of the quartz substrate were deposited gold electrodes with thickness t~60 nm and diameter d~4 mm. A detailed description of the gas experimental setup is given elsewhere [24. In summary, the sensor was placed in a gas-test chamber, whose temperature was kept constant at 26 °C. The concentration of NO_2, flowing into the thermally-stabilized measurement chamber, was varied between 10-5000 ppm. The sorption ability of the soot layers was investigated after initial resonance frequency stabilization as a result of dry air scavenging. Afterwards, the desired NO_2 concentration was added in the chamber and subsequent gas sorption on the sensor surface was observed via resonance frequency downshifts. This process was monitored until the system reached dynamic equilibrium and the frequency fluctuations remained within ±0.5 Hz. Finally, the gas chamber was scavenged again and a frequency backshift was observed. During the gas experiments, the QCM's resonance behavior was monitored via frequency counter HM8123 Hameg instruments and all experimental data were recorded on a personal computer. The measurement accuracy was found to be ~0.1 Hz.

RESULTS AND DISCUSSIONS

Electrical characteristics of an uncoated and SH QCM in air

The measurements were carried out using two quartz crystal resonators, intended to operate as QCMs, with a resonance frequency f_r ~16 MHz, dynamic resistance R_S=16.5–18.5 Ω and Q-factor of 19385–22185. Table 1 summarizes these electrical characteristics in air, prior to and after superhydrophobization. The deposition of carbon soot causes a proportional frequency downshift in the range of 643–814 Hz, a decrease in the Q-factor to 7913–8292 and a corresponding dynamic resistance increase of 37.4–43 Ω.

Table 1. Electrical characteristics of 16 MHz QCMs prior to and after superhydrophobization

QCM №	QCM status	f_r (MHz)	Q factor	R (Ω)
1	Prior to	15.958339	19385	18.5
	After SH	15.957525	8292	37.4
2	Prior to	16.022646	22185	16.5
	After SH	16.022003	7913	43

Gas sensing properties of the SH QCM

The sorption properties of the carbon soot coatings were investigated for NO_2 concentrations in the range of 10–5000 ppm. The initial gas-sensitivity of the SH QCM was determined at a concentration of 100 ppm and its real-time frequency response is illustrated in Figure 1.

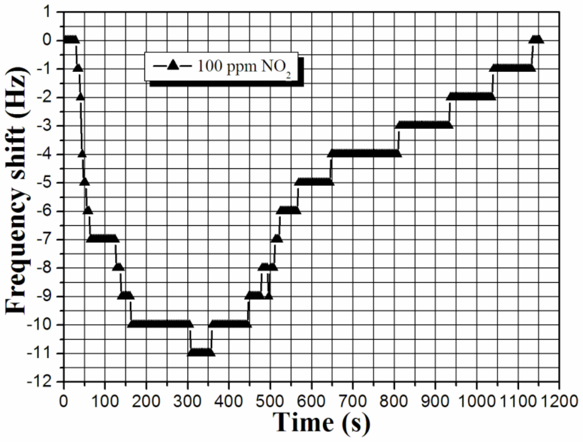


Fig. 1. Real-time frequency response of a SH carbon soot coated QCM at NO_2 concentration of 100 ppm.

As seen from Fig. 1, during the gas sorption there are two main areas, namely fast and slow one. In the first 52 s, the resonance frequency decreases with 7 Hz, while in the next 242 s the changes are within 4 Hz. The measured sorption rate is 2.19 Hz/min, which corresponds to 2.65 times faster process of sorption compared to the desorption one (~0.85 Hz/min). Similar fast and slow areas are registered when the adsorbed NO_2 gas is flushed away with a dry air flow. At the beginning of desorption, the resonance frequency recovers with 7 Hz for 300 s, while for the next 500 s the frequency shift is only 4 Hz.

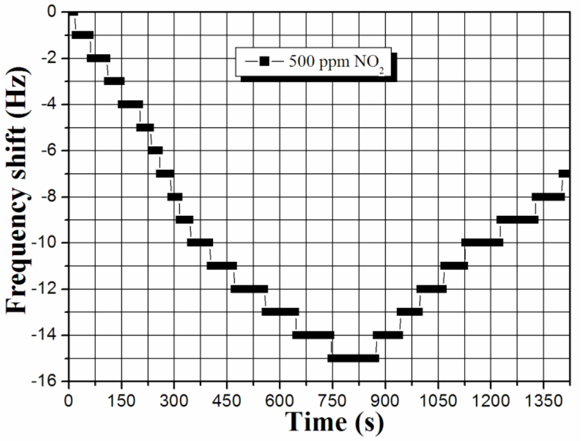


Fig. 2. Time-frequency characteristic of a SH QCM towards NO_2 concentration of 500 ppm.

Figure 2 represents the time-frequency characteristic of the SH QCM at higher NO_2 concentrations of 500 ppm.

In this case, the desorption rate is very slow (0.33 Hz/min); therefore, the recovery of resonance frequency is terminated at 1400 s. As evident from Figs. 1 and 2, the increased gas concentration (from 100 to 500 ppm) leads to an increase in the time for which the sensor system reaches dynamic equilibrium. This is expected since more gas molecules provided in the test chamber, more molecules would be adsorbed at the expense of a longer sorption time. The sorption-desorption analyses for the above range of gas concentrations are conducted for a period of 12 min. Figure 3 shows the resonance behavior of the SH QCM towards the entire NO_2 concentration range of 50-5000 ppm.

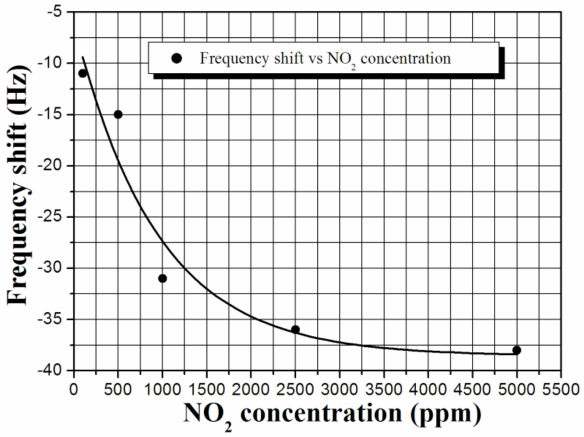


Fig. 3. Resonance frequency shift of a 16 MHz SH QCM towards NO_2 concentrations in the range of 50-5000 ppm.

For the chosen gas range, the SH QCM exhibits exponential resonance behavior with an overall downshift of 38 Hz. At low concentrations, up to 500 ppm, the sorption process is reversible and the sensor system recovers its initial electrical parameters (f_r, R_S and Q-factor). However, at higher concentrations (above 500 ppm), the sensor responds to the gas analyte, but the recovery time is significantly slower (0.33 Hz/min). These results reveal that the SH carbon soot coated QCM is appropriate for multiple measurements at low NO_2 concentrations, while above 500 ppm the sensor system can be used only for single NO_2 detection. For the sake of completeness, the coating's wettability was verified again through static contact angle, contact angle hysteresis and roll-off angle measurements. The obtained numerical values were 153 °, 1 ° and 4 °, respectively, thereby showing that after several sensor cycles, the layer is still superhydrophobic and shows no aging.

Humidity sorption and surface-characterization of the SH QCM

In order to validate the hypothesis that superhydrophobicity mitigates the condensation of water vapor on solid surfaces, further experiments were performed. The humidity-frequency responses of the SH QCM and a WO_3 coated hydrophilic QCM were recorded after saturation in a dry synthetic air flow and subsequent exposure to 45 % ambient humidity, and temperature T of 25 °C. The inclusion of a hydrophilic QCM allowed us to assess the extent to which superhydrophobicity inhibits the sorption of water vapor. Figure 4 shows the real-time frequency response of both devices towards 45 % RH.

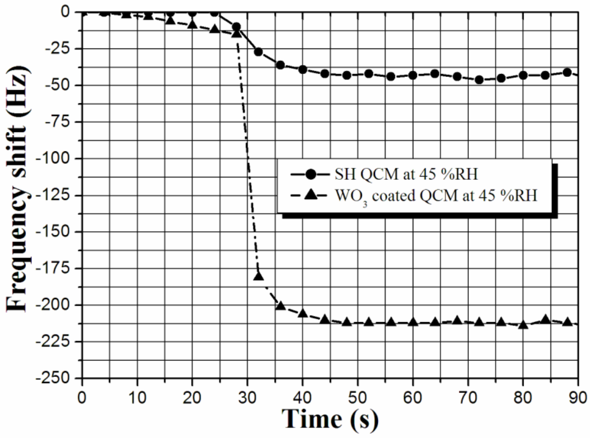
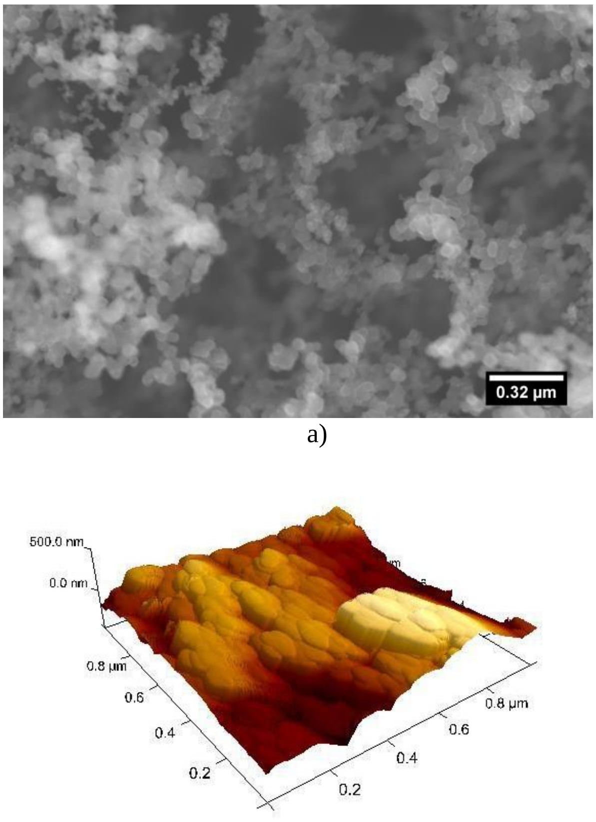


Fig. 4. Humidity-frequency response of a SH QCM and a WO_3 coated QCM in dry synthetic air and after exposure to 45 % RH.

As evident, upon exposure to 45 % RH and T ~25 °C, the resonance frequency of the SH QCM shifts down with approximately 45 Hz, against 212 Hz reduction for the WO_3 coated QCM. These data indicate ~5 times higher humidity sensitivity of the latter in comparison with the SH QCM. Therefore, our sensor device may operate in "real-world" environmental conditions with negligible cross sensitivity to humidity of 1Hz/% RH. In turn, this would substantially improve its sensor performance towards those of the commonly used metal oxide film coated QCMs. These observations are in good agreement with the heterogeneous nucleation theory [20]. It states that at equal other conditions the process of condensation depends on the surface wettability. For hydrophilic surfaces the energy barrier determining the phase transition is low due to the high surface free energy. For the superhydrophobic coatings; however, the latter is low. Therefore, the energy barrier is sufficiently high to ensure low nucleation (condensation) rate [20].

To compare the moisture sorption capacity of soot layers with their surface morphology, we performed SEM and AFM analyses. Figure 5 a) and b) shows 2-D and 3-D images of the carbon soot coated sensor surface.



a)

b)

Fig. 5. a) 2-D SEM and b) 3-D AFM images of the carbon soot coated QCM.

The images above clearly illustrate that the soot precipitates on the crystal surface irregularly, forming islands and cavities in the nanometer scale. This leads to an irregular surface topography composed of nanospheres and nanocavities. The root mean square roughness (R_{rms}) of the non-polar soot layer is estimated to be 130 nm, which converts the sensor surface into a superhydrophobic one. Similar results are achieved in [23] and [25], where carbon soot is deposited on glass slides and underlying epoxy resin coatings.

CONCLUSIONS

In this paper we presented systematic experimental investigations on the gas sorption ability of superhydrophobic carbon soot coated QCMs. The surface characterization analyses show that the non-polar and rough soot coating alters the sensor surface into a superhydrophobic one. As a result, superhydrophobicity induces approximately 5 times lower humidity sensitivity of the carbon soot coated QCM compared to a WO_3 coated QCM. Furthermore, the SH QCMs demonstrate reversible gas sorption at low NO_2 concentrations, up to 500 ppm, and insufficient desorption at higher concentrations. These results validate the hypothesis that superhydrophobicity mitigates the sorption of water vapor on the sensor surface. In turn, this opens a new venue in chemical sensing for the development of QCM based NO_2 detectors with negligible cross sensitivity to the ambient humidity.

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ХИМИЧЕСКИ СЕНЗОР ЗА ОТКРИВАНЕ НА NO_2, БАЗИРАН НА СВРЪХХИДРОФОБНА КВАРЦОВА МИКРОВЕЗНА

К. Д. Есмерян, В. Георгиева, Л Вергов, Й. Лазаров

Георги Наджаков Институт по физика на твърдото тяло, 72, Цариградско шосе, бул 1784 София

Получена на 23 април, 2015, Ревизирана на 25 май 2015

(Резюме)

Изследвана е газочувствителността на 16 МХц Кварцови Микровезни (КМВ), покрити със слой от въглеродни сажди, спрямо различни концентрации на NO_2. Анализите от сканиращ електронен микроскоп показват, че саждите се характеризират с неправилна подредба върху сензорната повърхност, образувайки въглеродни наносфери разделяни от наноразмерни пори и празнини. Неполярната природа на въглеродните наночастици заедно със средноквадратичната награпавеност на покритието от 130 nm преобразуват кварцовата повърхност в свръххидрофобна, характеризираща се със стойности на ъгъла на омокряне и хистерезис на ъгъла на омокряне от съответно 153 ° и 1 °. Подобна конфигурация на покритието предизвиква 15 Хц понижение в резонансната честота на свръххидрофобната КМВ при ниски концентрации на NO_2 до 500 ppm. Освен това, сензорът демонстрира обратима газосорбционна способност в същия диапазон от газови концентрации. Последващото постепенно увеличение на количеството NO_2 до 5000 ppm води до допълнителен сензорен отклик от 38 Хц. Въпреки това обаче, след продухване със сух въздух сензорът възстановява своята честота с много ниска скорост (~0.33 Хц/мин.). В допълнение, при промяна на относителната влажност на въздуха с 45 %, свръххидрофобната КМВ понижава честотата си само с 45 Хц, докато нейният аналог покрит с WO_3 с цели 212 Хц. Тези резултати ясно показват преимуществото на КМВ покрита с въглеродни сажди, изразяващо се в това, че тя може да бъде използвана за постоянен контрол на съдържанието на азотен диоксид във въздуха, при пренебрежима чувствителност на резонансната й честота към промени във влажността на околната среда.