Research Article

Determining the Optimum Exposure and Recovery Periods for Efficient Operation of a QCM Based Elemental Mercury Vapor Sensor

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In recent years, mass based transducers such as quartz crystal microbalance (QCM) have gained huge interest as potential sensors for online detection of elemental mercury (Hg0) vapor from anthropogenic sources due to their high portability and robust nature enabling them to withstand harsh industrial environments. In this study, we determined the optimal Hg0 exposure and recovery times of a QCM based sensor for ensuring its efficient operation while monitoring low concentrations of Hg0 vapor (<400 ppb).

The developed sensor was based on an AT-cut quartz substrate and utilized two gold (Au) films on either side of the substrate which functions as the electrodes and selective layer simultaneously. Given the temporal response mechanisms associated with mass based mercury sensors, the experiments involved the variation of Hg0 vapor exposure periods while keeping the recovery time constant following each exposure and vice versa. The results indicated that an optimum exposure and recovery periods of 30 and 90 minutes, respectively, can be utilized to acquire the highest response magnitudes and recovery rate towards a certain concentration of Hg0 vapor whilst keeping the time it takes to report an accurate reading by the sensor to a minimum level as required in real-world applications.

1. Introduction

The rapid growth of industrialization in the last century has increased the emission of toxic metal species such as elemental mercury in the atmosphere [1–7]. It is of high importance to control the emission of these metal species from common industrial sources in order to reduce the advert effect they are having on the environment as well as human health. Recently, new and more stringent rules have been introduced by government and environmental bodies worldwide to limit the amount of mercury emitted from industrial processes. For example, the average daily mercury emission from cement kilns in Germany is proposed to be limited to 3.5 ppb [8].

In order to comply with these regulations, efficient mercury vapor measurement techniques need to be implemented on targeted industry sites. Furthermore, in order to evaluate the efficiency of these removal technologies, highly accurate and sensitive online mercury vapor sensor is required.

In recent years, it has been shown that the mass based transducer such as quartz crystal microbalance (QCM) possesses several major advantages over other commonly used elemental mercury (Hg0) vapor measurement techniques, which are typically based on atomic absorption spectroscopy (AAS) and atomic fluorescence spectrometry (AFS), and
so forth [9–20]. The QCM based Hg\(^0\) vapor sensors were found to be highly portable and selective and they do not require sample pretreatment which make them highly suitable for online monitoring of Hg\(^0\) vapor within industrial applications [10]. Moreover, the design and the selective layer of QCM based sensors can be altered to achieve even higher sensitivity and selectivity towards low concentrations of Hg\(^0\) vapor. We recently reported that a QCM sensor based on gold nanospikes [21] can detect Hg\(^0\) vapor concentrations down to ~2.5 ppb\(_v\), which is lower than the threshold mercury exposure limit of 5.6 ppb\(_v\) set by world health organization [22]. Due to their potential to be used as online or hand-held sensors, it is very important to study QCM based Hg\(^0\) vapor sensors extensively in order to achieve the best performance for Hg\(^0\) vapor detection.

The schematic of a typical QCM based gas sensor is shown in Figure 1. The sensor is usually fabricated by depositing two electrodes on both sides of a suitable piezoelectric substrate (i.e., AT cut quartz). A bulk acoustic wave is generated upon the application of an electric potential on one of the electrodes [23–26]. The sensing film can be deposited on the electrode or the electrodes themselves can be made of a material which is selective to target analytes. Crystallographic characteristics and the thickness of the substrate and the electrodes determine the resonant frequency (\(f_0\)) of the sensor. Any perturbation on the sensing film (which typically occurs through mass loading of targeted analytes on the sensing film) results in a shift of the resonant frequency (\(\Delta f\)) of the sensor. This shift in \(f_0\) is highly dependent on the amount of analyte that interacts with the sensing film and can be related by the Sauerbrey equation (1) [27]:

\[
\Delta f = \frac{2f_0^2}{A \sqrt{\rho \mu}} \Delta m,
\]

where \(\Delta f\) represents the shift in the resonant frequency, \(\Delta m\) is the change in the mass of the sensing surface, \(A\) is the active area of the QCM electrodes, and \(\rho\) and \(\mu\) are the crystal density and shear modulus of the piezoelectric crystal, respectively. It can be observed from (1) that the shift in \(f_0\) increases as the mass loading on the sensing film increases, which indicates that the shift in \(f_0\) is proportional to the concentration of the species being detected.

In the current study, we focused on the Hg\(^0\) vapor detection application of a QCM based sensor. Therefore, extensive experimental and analytical approach was taken to determine the optimum exposure and recovery period to be used in order to efficiently monitor low concentration of Hg\(^0\) vapor using QCM based sensors.

2. Experimental

2.1. Sensor Fabrication and Quality Factor Determination. The QCM based sensor was fabricated on an AT cut quartz substrate having a diameter and thickness of 7.5 mm and 166 μm, respectively. 100 nm of Au layer on a 10 nm Titanium (Ti) adhesion layer was deposited on both sides of the quartz substrate to function as electrodes as well as the sensing layer simultaneously. The deposition was performed using a Balzers e-beam (BAK 600) evaporator operating at 22°C. Both of the electrodes were circular shaped which were patterned by using a shadow mask. The diameter of the electrodes was 4.5 mm. A photograph of the fabricated sensor is shown in Figure 2(a).

A network analyzer (Agilent E5100A) was used to measure the frequency response and determine the quality factor of the fabricated sensor. Figure 2(b) shows the frequency response of the sensor at 2 kHz span around the center frequency (9.99909 MHz). The quality factor of the sensor can be calculated using [28]

\[
Q = \frac{\text{energy stored}}{\text{power loss}},
\]

where \(\omega = 2\pi f\). The quality factor of the fabricated sensor was calculated as 6410 (i.e., >2500), indicating the sensor is suitable for gas phase analysis.

2.2. Mercury Testing Setup. The Hg\(^0\) vapor concentration used in different experiments of this study was 365 ppb\(_v\). This particular concentration of Hg\(^0\) vapor was generated by setting the temperature of a NIST certified permeation tube (VICI) to 80°C. The Hg\(^0\) delivery system was also calibrated on site using a potassium permanganate (KMnO\(_4\)) trapping method. This involved capturing the generated Hg\(^0\) vapor steam within a train of impingers containing H\(_2\)SO\(_4\)/KMnO\(_4\) and analyzing the solution by inductively coupled mass spectroscopy (ICP-MS) afterwards. This was done in order to ensure the concentration of Hg\(^0\) vapor was correct. The chamber which housed the QCM sensor had volume of 100 mL and was made of Teflon and stainless steel. The sensor recovery was a one-step process involving the exposure of the sensor toward dry nitrogen (N\(_2\)). A constant flow rate of 200 sccm and an operating temperature of 30°C were maintained throughout the whole study. The operating temperature of the sensor chamber was kept constant using an active PID controller. Temperature fluctuations within ±0.5°C were observed; however, this did not affect the sensing
result due to the high temperature stability of AT-cut quartz. A Maxtek RQCM was used for oscillation as well as to monitor resonant frequency of the sensor.

3. Results and Discussion

3.1. Optimum Hg\(^0\) Vapor Exposure Time. The performance of the developed Hg\(^0\) vapor sensor for different exposure times was investigated by exposing the sensor towards 365 ppb of Hg\(^0\) vapor for a range of exposure period ranging from 10 to 120 minutes whilst keeping the recovery period constant at 60 minutes. The structure of the full test is shown in Figure 3(a). It can be seen that after every Hg\(^0\) vapor exposure period dry N\(_2\) was flushed to the sensor for a period of 60 minutes. This process was performed in order to desorb the Hg\(^0\) vapor molecules from the Au surface and thus allow the sensor to recover to its baseline frequency. Figure 3(b) shows the dynamic response of the sensor for the entire test. It can be observed that the Hg\(^0\) exposure resulted in a negative shift in the resonant frequency while the sensor was observed to return it to its baseline frequency during the recovery time.

Figure 4(a) shows the sensor’s response toward Hg\(^0\) vapor concentration of 365 ppb, for an exposure time of 30 and 120 minutes while the recovery period was kept constant at 60 minutes. The pulses shown were extracted from a set of continuous pulses which were measured using a fixed exposure and recovery time for at least 3 cycles. This was done in order to obtain stable performance of the sensors in the final cycle. It can be observed from Figure 4(a) that the sensor response profile between the two exposure periods is different when considering the first 30-minute exposure period. This was mainly due to the different initial state between the two conditions presented (i.e., see Figure 3(b)). This can be further justified from Figures 4(b) and 4(c). That is, it can be observed from Figure 4(b) that the last pulse of 30-minute exposure and 60-minute recovery period cycles has the same adsorption response profile as the first pulse of 40-minute exposure and 60-minute recovery period cycle due to the same initial state of the sensor. This is further confirmed in Figure 4(c) where it can be observed that the last pulse of 90-minute exposure and 60-minute recovery period responds similarly as 120-minute exposure and 60-minute recovery period. Figure 4(d) shows the response magnitudes of the
Figure 4: (a) Sensor’s dynamic response toward Hg⁰ vapor concentration of 365 ppb, exposed for 30 and 120 minutes; (b) 30 and 40 minutes; and (c) 90 minutes and 120 minutes, all having a constant recovery time of 60 minutes. (d) Sensor’s response magnitude towards 365 ppb, of Hg⁰ exposed for 10 to 120 minutes with a recovery time of 60 minutes.

sensor toward the same Hg⁰ vapor concentration (365 ppb) for different exposure periods ranging from 10 to 120 minutes and a constant recovery period of 60 minutes. The response magnitudes of the last pulses for each Hg⁰ vapor exposure and recovery cycle were considered for analysis. The final pulse of each cycle was chosen as it allowed for the sensor to reach stability thereby resulting in desorption of the adsorbed Hg⁰ molecules from the Au surface and thus reducing the impact of a preceding pulse on the characterization of the following Hg⁰ exposure cycle. It can be observed from Figure 4(d) that the sensor’s response magnitude increased rapidly when the Hg⁰ vapor exposure time was increased up to 30 minutes. However, it can also be observed that the sensor’s response magnitudes did not vary significantly when the Hg⁰ vapor
exposure time was increased beyond 30 minutes. This observation indicates that the processes of Hg-Au amalgamation and diffusion of Hg atoms into the Au surface are relatively high up to a period of 30 minutes; however, they are reduced significantly beyond the exposure period of 30 minutes due to the Au surface reaching saturation. Therefore, no significant increase in response magnitudes was observed when the Hg\textsuperscript{0} vapor was exposed for more than 30 minutes. The initial Hg\textsuperscript{0} sorption kinetics (Figure 4(a)) is also observed to have changed (slowed) at the exposure time of 120 minutes due to the higher content of the mercury that was already on the surface from the preceding two cycles of the same pulse (i.e., having 120-minute exposure and 60-minute recovery periods).

3.2. Optimum Hg\textsuperscript{0} Vapor Recovery Time. In order to determine the optimum recovery time of the QCM based Hg\textsuperscript{0} sensor, the sensor was exposed towards Hg\textsuperscript{0} vapor concentration of 365 ppb\textsubscript{v} for a period of 30 minutes while the recovery period was varied within a range of 10 to 90 minutes. A period of 30 minutes was chosen as the Hg\textsuperscript{0} vapor exposure time as it was determined to be the optimum time from the previous test (Section 3.1) at which the saturated response magnitude was achieved at a low turnaround time. The test structure for determining optimum recovery period for QCM based Hg\textsuperscript{0} vapor sensor is shown in Figure 5(a).

The dynamic response of the sensor throughout the test can be observed from Figure 5(b). It can be observed that each exposure and recovery cycle was repeated 3 times before the next cycle started. The sensor’s dynamic response for 30 minutes exposure toward Hg\textsuperscript{0} vapor concentration of 365 ppb\textsubscript{v} employing three different recovery periods of 70, 90, and 120 minutes can be seen in Figure 6(a). It can be observed that the sensor exhibited a response magnitude of ~17.5 Hz when Hg\textsuperscript{0} exposure and recovery periods were 30 and 70 minutes, respectively. It can also be observed that the sensor’s response magnitude rose to ~19 Hz when the recovery period was increased to ~90 minutes while keeping the same Hg\textsuperscript{0}
vapor exposure period. Interestingly, the sensor’s response magnitudes did not vary significantly when the recovery period was further increased to 120 minutes.

A clearer view of sensor’s adsorption and desorption magnitudes for the different recovery periods ranging from 10 to 120 minutes can be observed from Figure 6(b). Here, it should be noted that the sensor’s desorption magnitudes were taken from the end of the recovery periods. It was interesting to observe that a ~23 Hz response magnitude was observed for a 30-minute exposure and 60-minute recovery periods pulse (Figure 4(d)) while in Figure 6(b) a ~18 Hz response was observed for the same exposure and recovery conditions. However, the difference arises from the preceding pulse cycles that were run for each condition. That is, the reduction in response magnitude for recovery period test was observed because the preceding recovery periods (i.e., 50 minutes) were not efficient enough for the sensor to release the adsorbed Hg vapor molecules from Au surface as opposed to the longer recovery period (60 minutes) used in all the pulses of the exposure test (Figure 3(a)). It can be seen from Figure 6(b) that the sensor’s adsorption and desorption magnitudes increased significantly up to 90 minutes even though the Hg vapor exposure period was kept constant at 30 minutes. It can also be observed from Figure 6(b) that while the sensor has high recovery efficiency for most of the recovery times tested the 90-minute recovery period showed to have more than 90% recovery efficiency while exhibiting maximum response magnitude towards Hg vapor. Overall, the results indicate that at least 90 minutes of recovery period is needed to acquire the highest possible response magnitudes as well as the recovery efficiency from the sensor while detecting low concentrations of Hg vapor without jeopardizing sensor’s response time. Getting a higher response magnitude and the recovery efficiency is particularly important as it will enable the sensor to have high sensitivity and thereby result in the efficient detection of low concentrations of Hg vapor in industrial processes.

4. Conclusion

The Hg vapor sensing performance of a QCM based sensor was investigated for different Hg vapor exposure and recovery periods. The developed sensor was based on an AT-cut quartz substrate containing thin Au-film substrate on both sides. The sensor was tested towards Hg vapor concentration of 365 ppbv, while the Hg vapor exposure and recovery periods were varied between 10 and 120 minutes. The overall results indicate that 30-minute Hg vapor exposure and 90-minute recovery periods can be utilized to achieve the highest response magnitudes and recovery efficiency from the sensor while keeping the turnaround time in a minimum level for real-world applications.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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