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Electro-deposition of Gold Nano-Structures on Gold Quartz Crystal Microbalance (QCM) Electrodes for Enhanced Mercury Vapour Sensitivity in the Presence of Interferent Gases

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Abstract — Gold electrode Quartz Crystal Microbalances (QCMs) were used as transducing platform to detect and sense elemental mercury (Hg) in gas phase. The enhanced sensitivity, resulting from the electro-deposition of gold nano-structures on the surface is shown to increase the response magnitude (RM) of the sensors in the presence of ammonia and humidity interference. The concentration of NH₃ and H₂O was varied in the range 590 to 1770mg/m³ and 4.2 to 10.4mg/m³, respectively. A constant gas flow of 200sccm, balanced in nitrogen was used as the carrier gas. The RM for Hg was enhanced by creating nano-structures on the sensor's gold electrodes via electro-deposition of gold in a lead acetate electrolyte. The results presented are a critical step in the development of a cheap regenerable and reliable sensor for measuring Hg in the presence of interferents gases commonly found in industrial applications.

Keywords – Electro-deposition, QCM, gold, mercury-sensing, ammonia, humidity, interference.

I. INTRODUCTION

Quartz crystal microbalances (QCMs) have gained a considerable interest for gas phase sensing [1,2] due to their stability, robust nature and simple operation. In 1959, Sauerbrey showed [3] that for an ideal layer of foreign mass deposited on the active surface of a QCM, a measurable change in frequency (Δf) is proportional to the deposited mass (Δm) on the surface, if the resonator is operated in air or vacuum:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{c_{66}\rho_q}} \Delta m = -S_f \Delta m \quad (1)$$

where S_f represents the integral mass sensitivity or Sauerbrey constant and is proportional to the square of the fundamental frequency, f_0 . The active surface area is denoted by A and c_{66} and ρ_q are material properties of the quartz crystal.

It is well understood from the literature that Hg adsorbs on to Au [4, 5] and forms an amalgam over time [6]. For mercury vapor sensing purposes, it is important to obtain a high

sensitivity when using a QCM in the presence of interferent gas species. Increasing the active surface area of the QCM electrode is thought to reduce the required exposure time of the sensor towards Hg vapor. The reduced exposure decreases the amount of Hg amalgamation, increasing the QCM's ability to regenerate itself by desorbing most of the adsorbed Hg at the conclusion of the sensing process.

In this work, the mass sensitivity of a QCM was improved by increasing the surface area of the gold electrodes via electro-deposition of nanostructure Au, using a process similar to that of Noort et. al. [7] and Imamura et. al. [8]. With this method, we have achieved approximately two to three times larger response magnitude (RM) towards Hg than non-modified Au QCM electrodes. These nano structures are shown to enhance the signal for Hg sensing, even in the presence of interfering gases such as ammonia and humidity.

II. PREPARATION OF QCM CRYSTALS

The two electrodes on either side of the quartz crystal were fabricated with a 100nm thin film of gold deposited over a 10nm Ti adhesion layer by e-beam evaporation. A non-modified crystal served as a control, while several others were set aside for surface modification by electro-deposition.

The electro-deposition was performed using an electrolyte solution containing 27.18g/L hydrogen tetrachloroaurate (III) hydrate and 1.77g/L lead(IV) acetate (from Sigma-Aldrich, Australia). A potential of -2V was applied between the two electrodes of the crystal (Cathode) and Au foil (anode) for 30 – 120s. This insured that Au nano-structures were formed on both Au electrodes of the QCM.

III. EXPERIMENTAL PROCEDURE

The QCMs were used as the frequency determining element in an oscillator circuit. An Agilent (53131A) frequency counter was used to measuring the resonant frequency change. A constant flow rate of 200sccm during all stages of testing was provided by a specially developed 4 channel mass flow controller system, while data acquisition was performed via a conventional desktop computer. The different Hg concentrations were generated by controlling the permeation tube temperature (P/N 137-100-0030-S56-C90), which were

purchased from VICI AG International, TX, USA. The Hg concentrations were calibrated using KMnO_4 (Sigma Aldrich, Vic, Aust.) trapping method and analyzed by ICPMS (Inductively coupled plasma mass spectroscopy). The three Hg concentrations the sensors were tested towards were 3.65, 5.70 and 10.55 mg/m^3 . The interferences were tested by introducing the interferent species to the sensors at all times during and after Hg exposures. The chamber temperature was maintained constant at 55°C.

IV. RESULTS AND DISCUSSION

Upon experimenting with the time of electro-deposition, the optimum time was found to be 30s providing the highest Quality – factor for the QCM transducer. Higher electro-deposition times were found to increase the loss of energy and so stop the oscillation of the QCM. Figure 1 and 2 show both the Secondary Electron Microscope (SEM) and Atomic Force Microscope (AFM) images of the non-modified and modified via electro-deposition Au electrode surfaces after exposure to mercury, ammonia and humidity.

Figure 1. SEM images of A) Non-modified surface after exposure to Hg and B) Electrodeposited surface after exposure to Hg

Figure 2. AFM images of A) Non-modified surface after exposure to Hg and B) Electrodeposited surface after exposure to Hg

The SEM images confirm the growth of nano-structure grains of around 50 to 250nm in size, after electro-deposition. The electro-deposited structures (Fig.1B) seemed to be coming out of the surface while the polished surface (Fig. 1A) seemed to have similar but smaller sized grains compared to the electro-deposited film. These “bead” type structures are about 20 to 50nm in size. AFM characterization (Fig. 2) of same surfaces indicates that the mean roughness is increased by a factor of 11.5 between the electro-deposited and non-modified surfaces, resulting in a 45% increase in surface area after electro-deposition.

The fundamental frequencies of the modified QCM, before and after the electro-deposition process, were logged. From

these data, using equation 1, it was found that the Au deposited on the QCM Au electrode was approximately 887 $\mu\text{g/cm}^2$. It is illustrated from figure 3 that the surface physical state has not changed significantly compared to the non-modified QCM Au electrode.

Figure 3. XRD spectra of Non-modified surface (line, bottom) and Electro-deposited surface (dashed, top)

Both the non-modified and electro-deposited Au surfaces were then exposed to Hg. The dynamic responses of the two QCMs are shown in figure 3A and 3B. The results illustrate that the modification via electro-deposition has increased the QCM affinity for Hg compared to the non-modified QCM.

Figure 4. Dynamic response of non-modified (line) and Electro-deposited (dashed) sensors towards Hg A) in nitrogen, and B) Response magnitude of Non-modified (line, triangles) and electro-deposited (dashed, squares) exposed to varying concentrations of mercury

It is well known that sensitivity is analyte concentration dependent [9, 10]. The sensitivity of the electro-deposited device is shown to be 157, 180 and 212% larger than the non-modified for the three tested concentrations of 3.65, 5.70 and 10.55mg/m³ Hg, respectively. Thus, it appears that the electro-deposited sensor operates in a different non linear region than that of the non-modified QCM. One would expect that due to the increased surface area of 45% from AFM data, we would expect a 45% increase in the mass adsorbed on the gold surface. From Sauerbrey equation, since Δf is proportional to Δm , a 45% increase in RM towards pure Hg of any concentration would be expected. Therefore the increase in response is not purely due to surface area increase reported by AFM. It is thought that electro-deposition process may have developed greater number of grain boundaries and defects. This assumption could then agree with the proposal of George et al [11] that the rougher film substrates promote diffusion of mercury into the films' grain boundaries. The non-modified sample is simply gold on polished quartz with Ti as the adhesion layer and is a film that is very flat and contains uniform grains and compact grain boundaries. Therefore, there are fewer sites available for mercury to occupy on the non-modified sample and hence a smaller RM is observed.

Even though the response of the electro-deposited QCM drifts down significantly compared to the non-modified QCM, the RM of the electro-deposited sensor was more repeatable over the four pulses for each concentration of Hg in figure 4A (within +/- 0.6%) than the non-modified sensor (within +/- 1.7%). From here on, only the results from the electro-deposited QCM is reported since it is found to be much superior in terms of response and repeatability over the non-modified QCM.

The modified sensor was tested against Hg in the presence of humidity (4.2 and 10.4mg/m³) acting as one of the main interferent gas (figure 5). It was found that the effect of humidity rises with increasing Hg concentrations. At a humidity concentration of 4.2mg/m³ and a Hg concentration of 3.65mg/m³, the RM of the electro-deposited sensor decreased by 5.9% leading to the sensor reporting 5.9% lower concentration.

Figure 5. Response magnitude of electro-deposited QCM exposed to varying concentrations of mercury and humidity

It is noted that a larger drop in RM occurs due to the NH₃ interferent (figure 6). That is, at Hg concentration of

3.65mg/m³ and ammonia concentration of 590mg/m³, the electro-deposited surface had dropped 17% in RM. At the higher ammonia concentration of 1770mg/m³, the drop in RM increases to 21%.

While keeping ammonia at 1770mg/m³ and increasing the Hg concentration, the reduction in RM seems to decrease by 17.5%. It was also observed that the reduction in response magnitude does not reduce with decreasing ammonia concentration.

Figure 6. Response magnitude of electro-deposited QCM exposed to varying concentrations of mercury and ammonia

By examining the response of electro-deposited sensor from figures 5 and 6, we observe that ammonia exposure had a bigger RM reduction affect as compared to humidity. This behavior may be explained from the work of Bilic et al. [12] who have reported high adsorption energy of ammonia on the Au (111) surface. They suggest the absence of covalent bonding between the gold and ammonia and suggest that the interaction is dispersive with some contribution from polarization. In their work, Kay et al. [13] studied the influence of adsorbate-adsorbate hydrogen bonding of NH₃ and H₂O on Au (111) and stated that repulsive interactions occur between acidic hydrogen atoms on adjacent NH₃ molecules and that H₂O binds more strongly to itself than to the Au substrate. Their observation explains the reasoning behind greater reduction in RM of the Au electrode QCM sensors upon exposure of ammonia over humidity. Water molecules are easily desorbed, from Au and its bound counterpart H₂O molecules, off to the nitrogen atmosphere whereas NH₃ molecules are more strongly bound to the Au substrate. Therefore it can be assumed that ammonia is not desorbed from the surface to the extent of humidity desorption and therefore the ammonia may work as a barrier for further Hg to adsorb on the surface resulting in reduced RM. Surface-enhanced Raman spectroscopy (SERS) study have been used in the past to show that even though ammonia does adsorb on gold, no irreversibly adsorbed ammonia species are formed at the gold electrode [14]. Therefore, ammonia is expected to completely desorb from the gold surface in the recovery period where only nitrogen gas is allowed in the sensing chamber.

In the final stage of the experiment, the electro-deposited sensor was exposed to Hg in the presence of both H₂O and NH₃ interferents. The QCM responses are presented in figure 7 below. It is observed that once an exposure of an interferent mixture occurs and reduces the RM of the modified sensor

towards Hg, no further reduction is observed when different concentrations of interferent mixtures are exposed. Upon the exposure of Hg in the presence of mixed interferents for the first time, the electro-deposited sensor reduced in RM by 21%. This is similar to the reduction observed when exposing only ammonia as the interferent gas (figure 6), indicating again that most if not all reduction in RM occurs due to ammonia.

Figure 7. Response magnitude of electro-deposited QCM exposed to varying concentrations of mercury, humidity and ammonia

After the initial interferent exposure cycle, further exposures at different interferent concentrations only gave an error of 2.4% for the electro-deposited QCM. This suggests that the Au electrode surfaces reaches equilibrium and becomes stable towards interferents. That is, once the sensors are calibrated against different concentrations of Hg in the presence of interferent gases mentioned, an error of ~2.4% would be expected from there on in, due to the fluctuations of interferents concentration in the application of an online Hg sensor.

V. CONCLUSION

The electro-deposited sensor was observed to have significantly larger response magnitude towards gaseous elemental mercury than the non-modified sensor. The sensitivity increase of the electro-deposited sensor was found to be Hg concentration dependent and so it appeared that the electro-deposited sensor operated in a different non linear region than that of the non-modified QCM. However, a drift in the response of the electro-deposited sensor was observed. The sensors were found to be more stable towards humidity, than ammonia as interferents while sensing gaseous elemental Hg. Ammonia as an interferent reduces the QCMs response magnitude by 21%. No significant further reduction in response magnitude upon exposure of NH₃ and H₂O interferents was observed following the first exposure of Ammonia, even when both interferents were present simultaneously. Experiments are under way to optimize the electro-deposition parameters in order to further develop the sensitivity and stability of the electro-deposited QCM towards Hg.

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