**Research Article**

# Gold thin film chemiresistor sensor for gaseous elemental mercury

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**Abstract**

The presence of gaseous elemental mercury (GEM) in the atmosphere has raised concern because it can cause serious health effects.  The largest anthropogenic source of atmospheric mercury in the Philippines is the artisanal small-scale gold mining (ASGM) sector, which accounts for about 30% of the country's annual mercury discharge.  There is therefore a need for a portable monitoring system for GEM that can be employed in the ASGM areas.  In this study, a gold thin film electrode was used as chemiresistor mercury sensor.  Interaction of mercury with the gold thin film produced changes in the resistance of the film that were dependent on the amount of mercury present. These changes can be monitored through the output voltage of the Wheatstone bridge circuit that was incorporated in the sensor.  The surface of the thin film can be regenerated through thermal desorption of the adsorbed mercury.  It is capable of detecting Hg vapor levels from 0 to 30 ng with good linearity (r = 0.9975) and with a detection limit of 1.77 ng. It yielded repeatable results as demonstrated for 10 ng Hg with rsd value of <10%. A prototype measurement system for gaseous elemental mercury based on this sensor was assembled.

**Keywords**: chemiresistor, gold thin film, mercury sensor

**Introduction**

The monitoring of atmospheric gaseous elemental mercury (GEM) is important because it has serious health effects (Pervez et al., 2010) and it is a cross-border pollutant (US EPA, 1997).  A background level of GEM has been found to exist in the Philippines (Ci et al., 2011).  The atmospheric GEM was attributed to emissions mainly from anthropogenic sources, of which the artisanal small-scale gold mining (ASGM) sector accounts for about 30% of the country's annual mercury discharge. Very high levels of GEM were detected in air in several mining areas, particularly during mining operations, based on measurements done in 2010 (Ci et al., 2011).

Data on the levels of atmospheric GEM near the ASGM sites is scarce. Regular monitoring of mercury in the environment has been carried out mostly on water systems. The regular monitoring of atmospheric GEM in the country is hindered by the limited availability of portable equipment for the measurement due to the relatively high cost of these instruments.

A number of low-cost compact devices have been developed for the convenient measurement of gaseous elemental mercury (GEM). Several GEM sensors monitored the change in the electrical conductivity of a gold film in the presence of mercury vapor (McNicholas et al., 2011; Sarajlic et al., 2013; Ruys et al., 2000; Sabri et al., 2009; Sabri et al., 2011; James et al., 2012; George and Glausinger, 1994), or through the change in the resonant frequency of a piezoelectric quartz crystal containing a gold sensing layer (Battistoni et al., 1996; Levlin et al., 1999; Lumex, 2012). An optical sensor has been assembled based on the change caused by mercury on the absorbance characteristics of a Langmuir-Blodgett film of gold nanoparticles (Krasteva et al., 2003).

The objective of this study is to develop a chemiresistor sensor for gaseous elemental mercury that can be employed for field measurements, particularly in ASGM areas. The sensor design is based on the well-known interaction of mercury with gold and the consequent change in the electrical conductivity of gold (San Esteban et al., 2007; Brown et al., 2008). The change in resistance was found to be dependent on the concentration of the mercury vapor in the gaseous mixture. The analytical performance of the sensor was established and correlated against a portable Hg Analyzer.

## Methods

*Gold thin film sensor.* The gold thin film sensor was custom-fabricated at the Barcelona Microelectronics Institute of the National Microelectronics Centre (IMB-CNM, Universitat Autonoma de Barcelona, Spain), based on a design described by Sarajilic et al. (2013). It is composed of a thin gold film (thickness = 100 nm) deposited on a silicon wafer chip (3.2 mm x 3.2 mm x 380 μm). The thin gold film was patterned into four meanders with 20 μm wide conductive lines, a heater with 40 μm wide conductive lines in the middle of the sensor and eight bonding pads. Two of the meanders positioned diagonally from each other are covered with SU-8 photoresist films and act as the reference while the other two exposed meanders act as the sensing electrodes. Each sensor chip was encapsulated in a TO5-8L header. The sensors were used as received with no further pre-treatment.

*Preparation of standard Hg-air mixtures.* A standard mercury gas mixture was generated by the Tekran 205 Mercury Vapor primary Calibration Unit. The unit generates saturated Hg-air mixtures at the set temperature after equilibration for 24 hrs. At 24ºC, the concentration of Hg-air in the gas generator's chamber is 18.82 ng/mL or 18,820,813.59 ng/m$^3$. Volumes of 0.10, 0.25, 0.35, 0.50, 0.75, 1.00, and 1.50 mL were withdrawn from the chamber using a gas tight syringe and introduced in the sensor cell, corresponding to 2, 5, 7, 10, 15, 20, 30 ng of Hg exposure, respectively.

*Assembly of instrumentation system.* The instrumentation system that was used for optimization and characterization consisted of an injector port, sensor cell and computer for data acquisition. The sensor cell was fabricated from a Teflon block (21 mm x 28 mm x 32 mm) which housed the gold thin film sensor. Argon was used as carrier gas that was allowed to flow into the sensor cell during blank readings and regeneration step. The change in electrical resistance of the chemiresistor was monitored through the output voltage of a Wheatstone bridge circuit. The output voltage was continuously collected and plotted using NI Signal Express™ 2013 (National Instruments).

*Measurement procedure.* A stream of ultra-high purity argon gas was allowed to flow through the sample cell for 15 min at a rate of 0.2 L/min and generated a baseline response. At the end of this period, the flow of gas was stopped and a certain volume of Hg-air mixture was introduced into the cell through the injection port using a gas tight manual syringe. After injection, both inlet and outlet valves were closed to trap Hg-air mixture inside the sensor cell. The sensor response was monitored until the response attained a steady state value. Sensor regeneration was achieved by applying 10V to the heater for 10 min with continuous flow of argon. Argon directs the desorbed Hg to the collecting chamber containing a mixture of $K_2Cr_2O_7$/$HNO_3$ solution.

*Sensor characterization and validation.* Using different volumes of the saturated Hg-air mixture, the sensor performance characteristics were determined: linearity, sensitivity, limit of detection, response time, reversibility and reproducibility. To validate the sensor performance, the sensor response to different volumes of Hg-air mixtures was correlated with the response obtained from a commercial mercury analyzer Lumex RA 915M. Morphological analysis was conducted using Park Systems NX10 Atomic Force Microscope (AFM). Different electrodes were used for each condition: before exposure to Hg and after exposure to 30 ng Hg and after regeneration.

*Prototype assembly.* A prototype of the sensor and the associated instrumentation was assembled based on the unmodified thin film gold sensor. The assembly incorporated the following units: (1) pre-concentration system; (2) sensor and signal processing unit; (3) sensor regeneration unit and (4) scrubbing unit.

## Results and discussion

*Sensor Response Profile.* The typical response profile of the sensor in one complete measurement cycle is presented in Figure. 1. The baseline signal was established with the gold thin-film sensor exposed to argon gas. Upon injection of the Hg-air gas mixture, the voltage dropped exponentially and reached a steady state within 5 min. The negative slope was due to the imbalance of the Wheatstone bridge causing $\Delta R < 0$ which may be due to the fabrication of the sensors. The introduction of Hg caused an increase in magnitude of the output voltage of the sensor but in a negative direction.
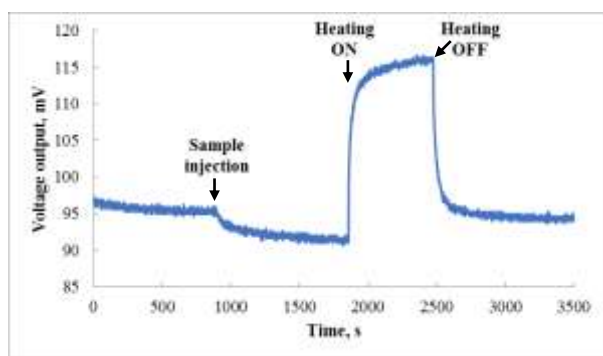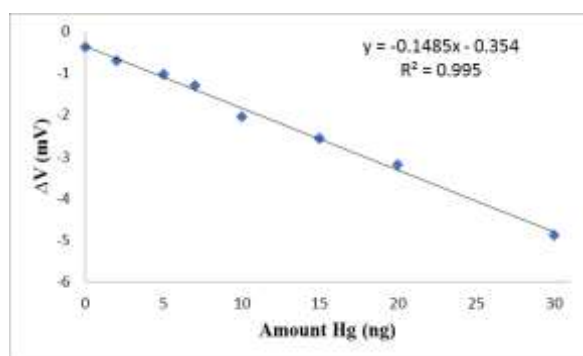


**Figure 1.** Sensor response profile



**Figure 2.** Sensor calibration curve

Activation of the heating element on the sensor chip caused the voltage to increase rapidly in less than a minute and gradually reached a constant value within 10 minutes. During the heating, the adsorbed Hg gas was desorbed and a fresh surface was regenerated. The amalgam formation of mercury with gold can be reversed by heating the gold thin film at a temperature between 110ºC to 150ºC (Raffa et al., 2006). The 10V potential that was applied across the heating element generated a temperature of 138ºC based on heater calibration results. It was proven sufficient to completely regenerate the sensor without causing melting of gold wire connections to the sensor chip bonding pads. Upon cooling, the baseline signal of the sensor was recovered within 5 minutes of exposure to argon. The recovery of the baseline indicates the reversibility of the sensor. The sensor response was shown to be repeatable, with a relative standard deviation of about 7% being observed for six successive runs.

*Effect of Hg concentration.* The approach chosen for the calibration of the sensor involved introducing different amounts, rather than concentrations, of Hg into the sensor cell. Different volumes of the saturated Hg-air mixture were introduced one at a time into the sensor cell. A very good linear (r = 0.9975) behavior was observed within the range from 0 to 30 ng levels of Hg (Figure 2). The sensor limit of detection is 1.77 ng Hg (n=8) that was determined through the injection of argon (zero Hg content) into the sensor cell. Repeatability of the sensor was determined by consecutive injections of 10 ng Hg which resulted to an rsd of 8.42% (n=8). The sensor was found to be useable up to 227 measurement cycles. This long lifetime of the sensor means that it will require fewer maintenance replacements when it is implemented in the field for remote measurements in monitoring stations.

*Surface analysis.* Surface analysis of the gold thin film through atomic force microscopy (Figure 3a) showed that it is made up of small clusters of gold ranging from 35 to 109 nm and large cluster of 699 nm. After exposure to Hg (Figure 3b), the surface of the gold thin film was altered into smaller clusters with sizes ranging from 51 to 164 nm. The change in the surface morphology can be due to the formation of gold-mercury amalgam. After regeneration (Figure 3c), the surface of the gold thin film was converted to larger clusters with sizes ranging from 31 − 285 nm. This signifies that the amount of heat liberated by the heater was sufficient to completely regenerate the sensor.

*Validation.* The performance of the gold thin film sensor was validated by comparing its response to that of a commercial mercury analyzer, Lumex RA-915M. The analyzer is a portable device that is based on differential Zeeman atomic absorption spectrometry. It does not require any pre-concentration steps and regeneration procedure. It can be used to measure mercury vapor at a range of 2 – 200,000 $ng/m^3$ at ambient conditions (Lumex, 2012)
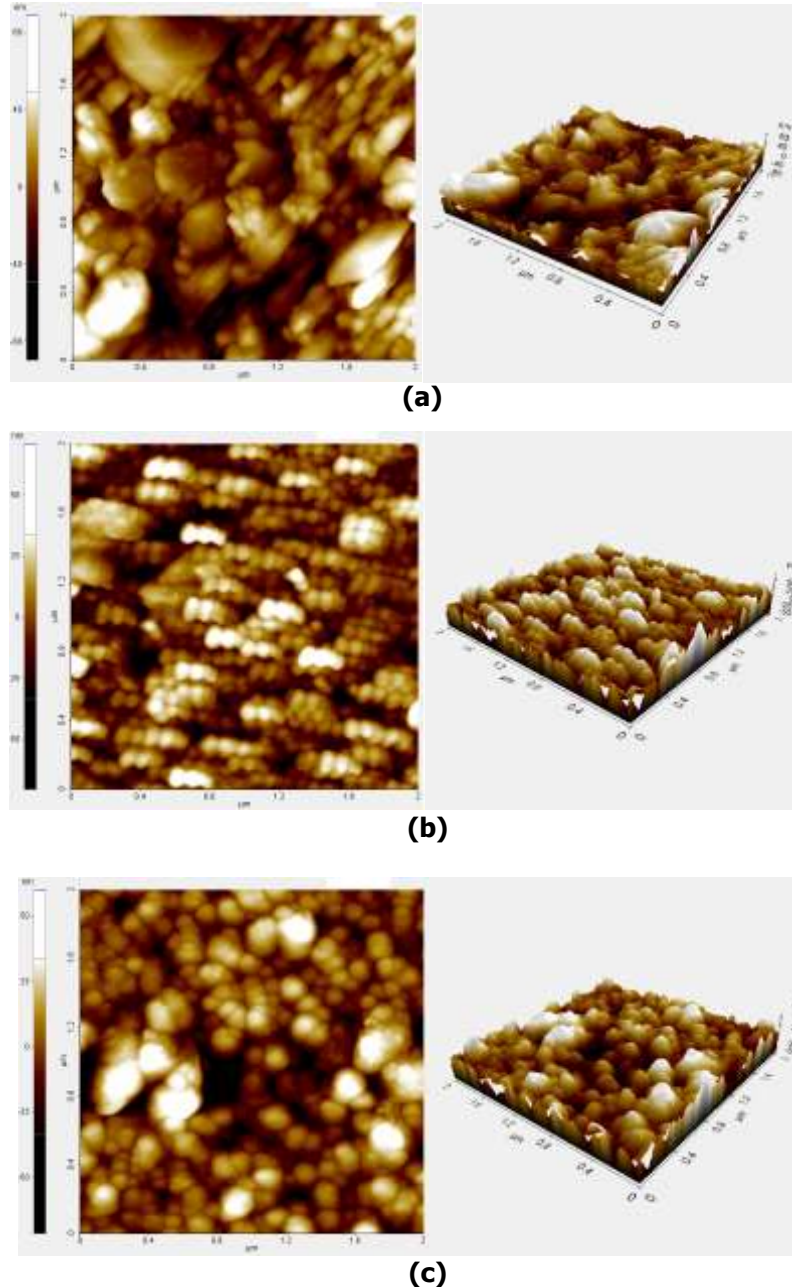


**(a)**



**(b)**



**(c)**

**Figure 3.** AFM images of gold thin film (a) before exposure to Hg,(b) after exposure to Hg and (c) after regeneration

The response of the gold thin film sensor showed a very good linear correlation with the response of the analyzer to different amounts of saturated Hg-air mixture (Figure 4). This behavior indicates the reliability of the sensor response with the different levels of mercury in a gas mixture.
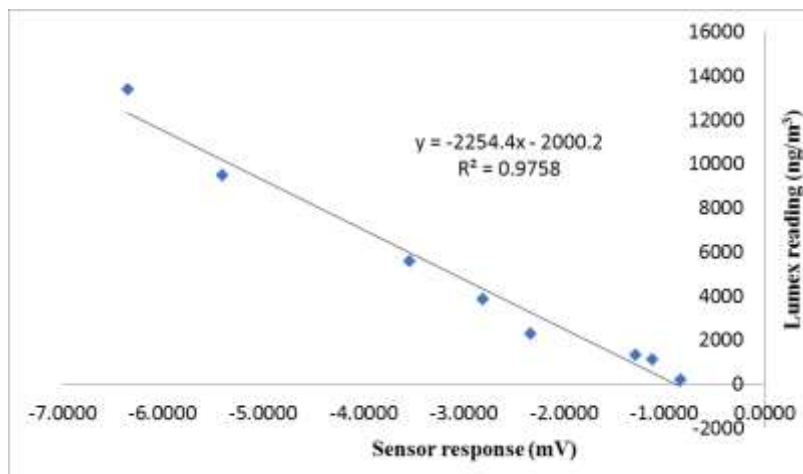
**Figure 4.** Correlation of the response of the gold thin film sensor and Lumex RA 915M

*Prototype development.*  To enable the measurement of low concentrations of GEM, a pre-concentration system was integrated into the field prototype. For a sample of air having a 10,000 ng/m$^3$ Hg concentration, the sensor cell having a volume of 1 cm$^3$ would be exposed to just 0.01 ng Hg which is below the detection limit of the sensor (1.77 ng Hg). The pre-concentration system consisted of a glass tube containing gold-coated silica that adsorbs the mercury from pumped air, and heating coils for the subsequent desorption step. The pump and the heating coils are driven by an Arduino-clone microcontroller which has been programmed to run the pump for one hour and then activate the heating coil for a period of 10 minutes. In effect, the pre-concentration system generates a small volume of gas with mercury levels that are above the detection limit of the sensor.
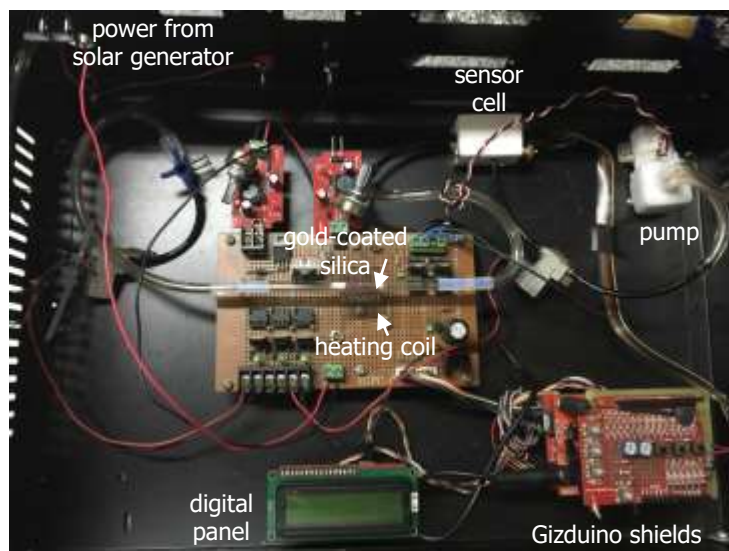


**Figure 5.** Photograph of the prototype assembly layout.

The thin film gold sensor is housed in a flow-through Teflon cell. It is connected to a 5 V voltage source, and it generates an output voltage signal which is related to the Hg content of the sample. A Gizduino board collects the output signal after 10 minutes of sample flow.  The generation of the readout is carried out through a program involving the parameters of the slope-intercept linear

equation of the calibration curve.  A heating unit is integrated in the sensor, together with the gold sensing thin film. It is powered by a 10 V power source which is driven by a Gizduino microcontroller. The voltage is applied for a period of 10 minutes, based on the parameters established during the characterization of the sensor. A scrubbing unit is included in the prototype design to prevent the preconcentrated Hg sample from escaping into and  polluting  the  atmosphere. The prototype is enclosed in a metal chassis and powered by a solar generator system. (Figure 5)

**Conclusion**

In conclusion, a satisfactory behavior has been observed from the assembled sensor system based on a thin Au film. The sensor with 100 nm gold layer thickness exhibits a linear behavior when exposed to different Hg vapor concentrations.  It can detect Hg vapor between 0 – 30 ng (r=0.9975) with an LOD of 1.77 ng. It was found to give repeatable results as demonstrated for 10 and 20 ng Hg with rsd values of <10%.  The sensor was found to be useable up to 227 cycles.  Field testing and improvement of the prototype design will be carried out in a succeeding project.

**Acknowledgement**

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