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Surface Acoustic Wave Mercury Vapor Sensor

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Abstract

Sensor Research and Development Corporation (SRD) has been contracted to develop and deliver a prototype instrument capable of the *in situ* detection and measurement of low levels of gaseous mercury for use in thermal waste treatment continuous emissions monitoring. The goal is to develop a fast, simple, inexpensive and reliable *in situ* sensor instrument for detecting and monitoring vaporized mercury that should be able to react to low (less than $5\text{ }\mu\text{g}/\text{m}^3$) levels of mercury vapor, should be site deployable and provide continuous data on either cumulative mercury exposure or instantaneous concentration.

Over the course of the reporting period, sensor responses were measured and analyzed for a wide range of sensing film thicknesses, operating temperatures, and adhesion layers. From this data, an optimal combination of those parameters was chosen. The film was then incorporated into the SAW sensing element, and rigorous testing has begun. To date, sensor responses to wide concentration ranges (0.7 ppb to 500 ppb) have been measured. Furthermore, a contract modification to include measurement of total mercury (both in elemental and reacted forms) has been requested and is expected to be finalized before the end of November, 1998. Finally, plans have been made for initial visits to the TSCA facility in Oak Ridge, TN and the University of North Dakota's EERC facility to gather information required for the construction of the prototype instrument and to discuss possible future collaborations and field testing.

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Executive Summary

Sensor Research and Development Corporation (SRD) is currently contracted to develop and deliver a prototype instrument capable of the *in situ* detection and measurement of low levels of gaseous mercury for use in thermal waste treatment process continuous emissions monitoring (CEM). The goal is to develop a fast, simple, inexpensive and reliable *in situ* sensor instrument for detecting and monitoring vaporized mercury that should be able to react to low levels of mercury vapor, should be site deployable and provide continuous data on either cumulative mercury exposure or instantaneous concentration.

The tasks embodied in the proposed work support the fundamental objective of achieving the design and fabrication of a prototype thermal waste treatment CEM. The work begins with the determination of the optimum operating temperature and film thickness for the sensing element. At this point, the sensing element will be designed and fabricated. Next, the sensing element will be rigorously tested in a laboratory environment to ensure that it meets certain reasonable success criteria. The next phase of the work involves the design and fabrication of a prototype instrument based around the mercury sensing element. When the instrument is completed, it will be tested in both the laboratory and in real-world applications to verify its operational capabilities.

Technical progress to date on the project include the following: A delivery system for gaseous mercury has been designed and constructed. A microheater and temperature control circuitry and software have been designed and implemented. Sensor responses have been measured and analyzed for a wide range of sensing film thicknesses, operating temperatures, and adhesion layers. An optimal combination of those parameters has been chosen. Rigorous testing of the new film is underway and will include exposures to wide ranges of gaseous mercury concentrations (0.5 ppb to 1 ppm), as well as exposures to possible interferent gases. A contract modification to include measurement of total mercury (both in elemental and reacted forms) has been requested and is expected to be finalized before the end of November, 1998. Plans have been made for initial visits to the TSCA facility in Oak Ridge, TN and the University of North Dakota's EERC facility to gather information required for the construction of the prototype instrument and to discuss future collaboration and field testing.

Introduction

This technical report for the period of April, 1998 through September, 1998 is an update on the technical progress of SRD's project for the development and delivery of an instrument for *in situ* measurement of gaseous mercury in thermal treatment processing facilities. The underlying sensing mechanism for gaseous mercury is based upon surface acoustic wave (SAW) technology with a thin gold film. A SAW delay line is used as an ultrasensitive microbalance. By coating the delay line with a thin gold film and configuring it as an RF oscillator, mass changes in the film can be measured by monitoring the oscillation frequency. Because of gold's strong interaction with mercury (amalgamation), this configuration can be used to sensitively detect gaseous mercury. Mercury can be driven from the film by heating it to a high temperature. Furthermore, by operating the device at an elevated temperature, the reaction kinetics of mercury amalgamation and desorption can be balanced so that an equilibrium surface mass can be quickly realized. The oscillation frequency then becomes a direct measure of the instantaneous mercury concentration. A second SAW delay line without a sensing film is also incorporated into the

device to act as a reference so that extraneous environmental effects which perturb both delay lines equally (i.e. temperature fluctuations) can be subtracted out.

Results and Discussion

Refinement of the Sensing Element

With the entire experimental apparatus and sensing element constructed, as described in the March, 1998 technical report, the next step was the determination of optimal film parameters for maximum sensitivity and minimum response time. A large matrix of experiments was performed, exposing dozens of sensing elements to 200 ppb doses of mercury in dry nitrogen under a variety of conditions. One of the parameters differentiating the films was their thickness; films of 50, 150, 400, 1000, and 2000 Å were tested. For each film thickness, two devices were tested for each of three different adhesion layers (50 Å chromium, 50 Å tungsten, and no adhesion layer). Although examination of the effects of the film adhesion layer were not initially planned, this work was necessary as it had a large effect. Each of these 30 sensing elements was tested at 25 different temperatures (for a total of 750 different tests), ranging from 30°C to 400°C. Although exhaustive results cannot be included for obvious reasons, many phenomena are described, and example response plots and summary plots are included below.

Figure 1 shows an example of a device response to 200 ppb mercury in dry nitrogen at temperatures ranging from 30°C to 200°C, as indicated. These tests were run on a 1000 Å gold film with a 50 Å tungsten adhesion layer. The response is plotted in terms of the ratio of the sensor frequency to the reference frequency (the reference is essentially constant). The periodic large decreases in frequency are caused by a rapid increase in film temperature to 200°C to “burn off” any remaining mercury after each response. The temperature is then maintained as indicated, and mercury is exposed to the device.

Surface Acoustic Wave Mercury Vapor Sensor

Figure 1. SAW response of 1000Å Au film on 50Å W to 200 ppb Hg⁰ in dry N₂ at varying temperatures.

One interesting phenomenon seen in this plot, as well as for all films 400Å and thicker on tungsten, is the decrease in frequency for the response at low temperatures. At higher temperatures (75°C and up) the response was manifested as an increase in frequency for all film thicknesses. The 150Å and 50Å films responded with increasing frequency for all temperatures tested. This phenomenon can be attributed to two opposing reactions of the SAW device to amalgamated mercury. First, the SAW responds by decreasing its frequency in proportion to the added mass absorbed by the film. In opposition, however, the SAW frequency increases in response to the mechanical stiffening of the film caused by the mercury interaction. Apparently at low temperatures on thicker films, the mass loading effect outweighs the stiffening. At higher temperatures and lower thicknesses the opposite is true.

Figures 2 and 3 show more detail for specific responses of Figure 1. As the Figures show, temperatures of 150°C and 175°C both show reasonable sensitivity and quick response times, with the lower temperature having more sensitivity and the higher temperature having better response time. At 175°C the response time is less than 5 seconds, as shown in Figure 3. At 200°C (not shown), the response time is less than 2 seconds, but the sensitivity is not adequate. At temperatures above 200°C, sensitivity was quite low for all films.

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Figure 2. SAW response of 1000Å Au film on 50Å W to 200 ppb Hg⁰ in dry N₂ at 150° and 175°C.

Figure 3. SAW response of 1000Å Au film on 50Å W to 200 ppb Hg⁰ in dry N₂ at 175°C.

In addition to film thickness and operating temperature, another important parameter affecting the device response turned out to be the adhesion layer. The responses shown previously utilized a 50Å layer of tungsten for proper adhesion of the gold film to the quartz substrate. Using a chromium adhesion layer, or none at all, however, yielded different results.

Chromium was the first adhesion layer tested, as chromium is used extensively in the semiconductor industry to promote adhesion between gold and quartz. While the resultant film showed excellent adhesion using conventional mechanical tests at room temperature, the sensor responses showed a rapid degradation with time. After careful experimentation it was discovered that this sensitivity decrease occurred only for devices which had been operated at temperatures of 200°C or higher. Devices which had never been operated over 200°C continued to respond well for some time, but eventually showed some gradual degradation, as well. After an extensive literature search, it was discovered that at high temperatures chromium diffuses through grain boundaries in the gold film, migrating to the surface. Upon reaching the surface of the film, the chromium is oxidized and forms a protective layer. Since the majority of the gold-mercury interaction takes place at the grain boundaries, the sensor response was significantly inhibited.

With that information, films with no adhesion layer were tested. While these films showed excellent response characteristics, the lack of adhesion between gold and quartz caused the film to migrate across the surface of the device when operated at high temperatures. The resultant film would alloy with the aluminum IDTs of the SAW device or would form small “balls” of gold, rather than a continuous film. The resultant device was less sensitive and not very stable.

This led to the search for a suitable adhesion layer which would yield highly sensitive and stable responses to mercury. Tungsten was chosen and the results demonstrate that it works well.

After collecting and evaluating data for 750 different sensor exposures, a set of device parameters has been chosen which yields the best results for the application at hand. Those parameters are a gold film thickness of 1000Å, a 50Å tungsten adhesion layer and an operating temperature between 150°C and 175°C. Both operating temperatures yielded adequate sensitivity and rapidity with the lower being more sensitive and the higher being faster.

Rigorous Testing of the Sensing Element

With the sensing element complete and optimal operating parameters defined, the next step, rigorously testing the device under normal operating conditions, is now underway. This testing will include an evaluation of the dynamic range of the device, including measuring the minimum detection limit, saturation detection limit, and linearity (resolution) of the sensor. The testing will also include exposures to mercuric chloride (HgCl_2), a common Hg(II) product. Possible interferent gases will be tested, as well, including H_2S , SO_2 , and water vapor.

The search for the minimum detection limit of the device has begun. Figure 4 shows the sensor response to repeated exposures of mercury at extremely low concentrations of 700 ppt and 1 ppb (~ 6 and $8 \mu\text{g}/\text{m}^3$). The temperature is held constant at 150°C (not ramped to 200°C between exposures as in the examples above), and the gas concentration is varied among 0, 0.7, and 1 ppb levels, as indicated. The much higher sensitivity levels compared to the 200 ppb exposures

shown above are due to changes in the device structure which result in enhanced surface coverage of the gold film. With ambient mercury levels of 50 to 300 $\mu\text{g}/\text{m}^3$ in typical thermal treatment process exhaust streams, this sensitivity should be adequate. Concentrations lower than 700 ppt are difficult to achieve with the current gas delivery system and available permeation tubes, but if necessary, the system can be temporarily modified to deliver these concentrations so that the ultimate minimum detection limit can be assessed.

Figure 4. SAW response of 1000Å Au film on 50Å W to 700 ppt and 1 ppb Hg^0 in dry N_2 at 150°C.

Site Visits

One important aspect of this development effort is a detailed knowledge of the application requirements and environment in which the sensor will operate. Toward this end, site visits have been planned at two typical facilities where the sensor may be used. The first site to be visited is the TSCA (Toxic Substances Control Act) incinerator in Oak Ridge, TN. Several other mercury CEMs have been tested at this facility, including the Perkin-Elmer Mercem®, which is currently being evaluated on site. The PI and an engineer from SRD plan to meet with James Dunn of the TSCA facility during the week of October 19, 1998.

Another site to be visited in the upcoming months is the University of North Dakota's Energy and Environmental Research Center (EERC). A meeting has been tentatively scheduled between the PI and EERC's Dennis Laudal during the week of December 7, 1998 to discuss possible collaboration on the project and use of EERC's testing facilities.

Conclusion

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As of October 1, 1998 SRD is working under the status of a no-cost extension to the project, pending implementation of the contract modification. This is expected to take about six weeks, and testing will continue in the mean time so that the project can remain on schedule.

In summary, the last reporting period has seen advancements in the understanding of the gold-mercury interaction, the development of an optimal sensing element, and the initiation of in depth sensor testing. With approval of the contract modification, the next five months will be spent rigorously testing the device's response to elemental mercury and mercuric chloride. Meanwhile, site visits and meetings will help in defining the application requirements for the prototype instrument.

List of Acronyms and Abbreviations

CEM	Continuous emissions monitor
cm ³ /min	Cubic centimeters per minute
EERC	Energy and Environmental Research Center
Hg	Mercury
Hg ⁰	Elemental mercury
Hg(II)	Divalent mercury
HgCl ₂	Mercuric Chloride
H ₂ S	Hydrogen Sulfide
MFC	Mass flow controller
ng/min	Nanograms per minute
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
RF	Radio frequency
SAW	Surface acoustic wave
SO ₂	Sulfur Dioxide
SRD	Sensor Research and Development Corporation
TSCA	Toxic Substances Control Act
µg/m ³	Micrograms per cubic meter