(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
16 April 2009 (16.04.2009)

PCT

(10) International Publication Number
WO 2009/049091 A2

(51) International Patent Classification:
G01N 27/407 (2006.01)

(21) International Application Number:
PCT/US2008/079416

(22) International Filing Date: 9 October 2008 (09.10.2008)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/978,696 9 October 2007 (09.10.2007) US

(71) Applicant *(for all designated States except US)*: **UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC.** [US/US]; 223 Grinter Hall, Gainesville, FL 32611 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BLACKBURN, Bryan, M.** [US/US]; 2300 S.W. 43rd Street, M1, Gainesville, FL 32607 (US). **WACHSMAN, Eric, D.** [US/US]; 5212 N.W. 16th Place, Gainesville, FL 32605 (US).

(74) Agents: **PARKER, James, S.** et al.; Saliwanchik, Lloyd, Saliwanchik, P.o. Box 142950, Gainesville, FL 32614-2950 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

(54) **Title:** MULTIFUNCTIONAL POTENTIOMETRIC GAS SENSOR ARRAY WITH AN INTEGRATED TEMPERATURE CONTROL AND TEMPERATURE SENSORS

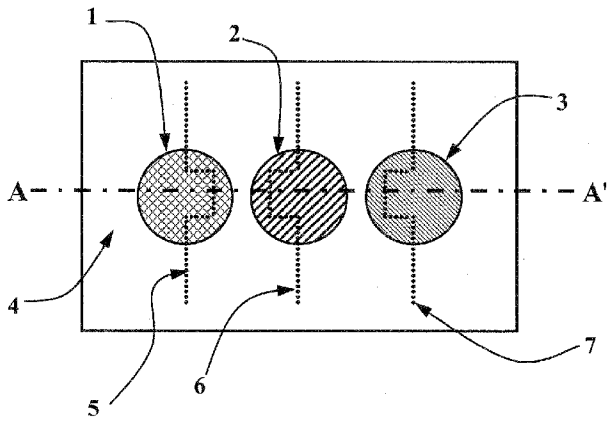

FIG. 1

(57) **Abstract:** Embodiments of the subject invention relate to a gas sensor and method for sensing one or more gases. An embodiment incorporates an array of sensing electrodes maintained at similar or different temperatures, such that the sensitivity and species selectivity of the device can be fine tuned between different pairs of sensing electrodes. A specific embodiment pertains to a gas sensor array for monitoring combustion exhausts and/or chemical reaction byproducts. An embodiment of the subject device related to this invention operates at high temperatures and can withstand harsh chemical environments. Embodiments of the device are made on a single substrate. The devices can also be made on individual substrates and monitored individually as if they were part of an array on a single substrate. The device can incorporate sensing electrodes in the same environment, which allows the electrodes to be coplanar and, thus, keep manufacturing costs low. Embodiments of the device can provide improvements to sensitivity, selectivity, and signal interference via surface temperature control.

WO 2009/049091 A2

DESCRIPTION

MULTIFUNCTIONAL POTENTIOMETRIC GAS SENSOR ARRAY WITH AN INTEGRATED TEMPERATURE CONTROL AND TEMPERATURE SENSORS

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims the benefit of U.S. Provisional Application Serial No. 60/978,696, filed October 9, 2007, which is hereby incorporated by reference herein in its entirety, including any figures, tables, or drawings.

BACKGROUND OF INVENTION

Potentiometric gas sensors based on measuring the potential difference between a semiconducting metal oxide and a noble metal pseudo-reference electrode in the same gas environment offer highly selective devices that are easily manufactured and can withstand harsh environments without degrading performance. Furthermore, they are insensitive to large swings in O_2 concentration, such as those that occur in a combustion exhaust. Such solid-state potentiometric gas sensors show great promise for detecting pollutants such as NO_x, CO, and hydrocarbons from ppb to ppm level concentrations for exhaust monitoring. They also may be used in other applications such as in the biomedical field for breath analysis.

Potentiometric gas sensors have an output voltage signal that can be measured in many different ways and can be used to determine individual gas concentration(s) in a gas mixture or that of a varying concentration of single species in the absence of other gases. The voltage difference between two electrodes, which make up an "electrode-pair", can be monitored as the potential at one or each electrode changes.

Potentiometric gas sensors are utilized by measuring the output voltage signal that can be used to determine individual gas concentration(s) in a gas mixture or that of a varying concentration of single species in the absence of other gases.

Solid-state potentiometric gas sensors with semiconducting metal oxide electrodes (such as p-type La_2CuO_4 (LCO)) have shown much promise for the monitoring of pollutant gas (such as NO_x) levels in combustion exhaust. They are sensitive to ppm levels of NO_x and

concentrations. However, the selectivity and cross-sensitivity of these sensors is currently inadequate for commercial application. A prime example of this is the inability to discriminate between NO and NO_2 (the primary components of NO_x). It is often important to know the concentration of each of these individual gases; however, most NO_x sensors cannot determine which of these species is present or determine their absolute concentration in mixed gas streams. In fact, poor selectivity hinders most solid-state pollutant sensors. Currently available devices for monitoring combustion exhausts and/or reaction byproducts are limited in several ways. Current devices detect only one gas species or detect multiple species only by utilizing expensive electronics to extrapolate the gas concentrations from the measurement or to take the measurement.

Current devices can require an air reference, which complicates the design, and/or have complicated manufacturing steps that increase cost.

A reference electrode is typically used to compare the changing EMF of a sensing electrode to an EMF that does not change (i.e., a reference state). A pseudo-reference is an electrode which can be used to compare all other sensing electrodes in a single gas environment. However, the pseudo-reference has an EMF that changes at the same time that the sensing electrodes are changing. Accordingly, a pseudo-reference does not actually represent a true reference state.

BRIEF SUMMARY

Embodiments of the subject invention relate to a gas sensor and method for sensing on or more gases specific embodiments pertain to a potentiometric gas sensor and method for sensing on or more gases. Additional embodiments are directed to amperometric and/or impedimetric gas sensors and method for sensing one or more gases. An embodiment incorporates an array of sensing electrodes maintained at similar or different temperatures, such that the sensitivity and species selectivity of the device can be fine tuned between different pairs of sensing electrodes. A specific embodiment pertains to a gas sensor array for monitoring combustion exhausts and/or reaction byproducts. An embodiment of the subject device related to this invention operates at high temperatures and can withstand harsh chemical environments.

Embodiments of the device are made on a single substrate. In other embodiments, several different single electrode-pair devices can be produced on separate substrates. The device can incorporate sensing electrodes in the same environment, which allows the

electrodes to be coplanar and, thus, keep manufacturing costs low. Embodiments of the device can provide improvements to sensitivity, selectivity, and signal interference via surface temperature control.

Embodiments of the subject device can have a single pseudo-reference. Other embodiments can use all of the electrodes as pseudo-references with respect to each other. The electrodes can be viewed as making up "electrode-pairs," which can be measured as a potential difference signal. The voltage difference between two electrodes (which make up an "electrode-pair") is measured as the potential at one or each electrode changes. Embodiments can also have as a reference another fixed voltage, such as that provided by a battery, other power source or the chassis of an automobile.

Sensing electrodes can be metals (e.g., Platinum or Gold), semiconductors (e.g. semiconducting oxides such as La_2CuO_4 or WO_3), or any other material showing sensitivity to a single or multiple gas species. Typically, a given sensing electrode material will have varying sensitivity (i.e., changes in EMF) and selectivity to one or many different gas species This depends on the temperature of each electrode and the difference in temperature between electrodes making up an electrode-pair. This will also depend on the concentration and chemical properties of the particular species interacting with the material. The degree of sensitivity and/or selectivity that changes depends on the material and its properties, gas species present, and the temperature. Since each electrode may be part of one or more "electrode-pairs," the number of measurable signals can be larger than the actual number of sensing electrodes.

The presence of more signals than actual number of electrodes can be an advantage in a device. Typically, with a greater number of signals the pattern recognition of multiple gas species becomes easier. The voltage response of electrode-pairs can be measured over a variety of known conditions, including exposures to one or more gas species concentrations, and these measurements can be used to interpret the measurements taken during exposures to unknown gas species concentrations (i.e., the sensor may be calibrated). Therefore, the result of having more signals than total number of electrodes means that a device will require fewer electrodes for the same or better selectivity. This, in turn, means reduced costs and the possibility of smaller devices.

The design of the sensor array can include, either as individual devices or together in a single device, two different "electrode-pair" schemes. One scheme uses multiple materials at the same time, which may be kept at the same and/or different temperature (using heating

or cooling methods). A device may also include multiple electrodes of the same material that are maintained at one or more different temperatures.

The electrodes of the same material may be kept at the same temperature if other features of the electrode, such as microstructure (e.g., grain size or surface roughness), size, shape, or thickness, are different. Again, the gas sensor array may utilize one of these schemes or both of these schemes in a single device (or multiple devices), depending on the application.

Any given sensing electrode material is typically sensitive to more than one gas species. This sensitivity varies with temperature and gas species. Therefore, one can measure a signal from two electrodes of the same material if they are modified in a way that alters the sensitivity of at least one of the electrodes making up an electrode-pair. The sensitivity of a given electrode material can be modified by differences in its microstructure, geometry, temperature, or other method which changes the local environment of the electrode to enhance or alter chemical (or electrochemical) reactions in a desired way. The same modifications may be used to yield a measurable electrode-pair made up of dissimilar materials.

To be cost effective, the device(s) can be made on a single substrate. Furthermore, the device(s) can have sensing electrodes in the same environment, which allows the electrodes to be coplanar (i.e., all on one side of the substrate) and, thus, avoiding complex designs which might increase manufacturing costs. The sensitivity and selectivity of these sensors varies with temperature. Therefore, the temperature of such device(s) can be controlled and enabled to be modified quickly if the ambient temperature changes or if the electrode temperature changes for any other reason.

In order to achieve a device that is able to monitor two or more gas species of interest, an array of sensing electrodes can be used. The array signals can then be entered into algorithms to determine the concentrations of individual species. Pattern recognition can be implemented to determine the concentrations of individual species. By improving selectivity, a device can have fewer sensing electrodes to effectively detect the same species as a device with more signals but increased cross-sensitivities. This can simplify the device and lower the power consumption and the cost of constructing the device.

Heaters can be utilized with the subject invention in order to control the temperature of one or more of the sensing electrodes. Such heaters can use one or more heating elements through which current can be driven to create heat so as to alter the temperature of the

sensing electrodes. The heating elements can use any conducting or resistive material (e.g., Platinum) which has the thermal and chemical stability necessary to keep it (and its performance) from degrading with time and in a harsh environment. The heating elements can act as resistors. The heat is produced via Joule heating, or passing electrical current through the heating elements. The heat generated is proportional to the square of the current multiplied by time. Additional embodiments can use a cooling apparatus to lower the temperature of the sensing electrodes. A variety of cooling techniques known to those skilled in the art can be incorporated into embodiments of the invention for this purpose.

Temperature control of embodiments of the subject devices can be accomplished in a number of ways. Precise control of temperature with minimal fluctuations is useful to achieving stable sensor signals. Therefore, thermal modeling can provide a way to design the temperature profile for the device. This information can be used when determining where to locate individual electrodes on the substrate of the array or how the temperature profile will change in varying gas flow velocities.

Surface temperature measurements can be difficult. Knowledge of the temperature of the sensing electrodes can enhance the device performance. The resistance of some metals, semiconductors, or other materials will change with temperature in a way which can be predicted by various mathematical models. After the data is fit to a model, software can easily calculate the surface temperature during sensor operation using the coefficients from the model and resistance measurements of the temperature sensor elements. In a specific embodiment, resistance measurements, or other temperature determining technique, can be applied to the sensing electrode, for example before or after the gas sensing measurement, in order to provide a value for the temperature of the sensing electrode. Additionally, temperature sensors that utilize changes in voltage (e.g., thermocouple) or capacitance as a detection method may also be integrated into the device.

Heating elements can be used not only to heat another object but also simultaneously as a temperature sensor. If the resistance of the heater can accurately be determined (e.g., using a four-wire method), then the temperature of the heating element (and thus that of the sensing electrode) can be calculated. Resistance typically increases as current is supplied to the heater because of Joule heating. This does not greatly affect the voltage or current measurements. That is to say, the measurements represent the actual current in the circuit and voltage drop across the heater. Therefore the calculated resistance, and hence temperature, of the heater represents the real value.

The heating element shape can be designed to ensure that temperature of any given sensing electrode is uniform, or, if desired, designed so that the temperature is purposefully nonuniform. The heating elements may be C-, spiral-, serpentine-shaped, or any other useful pattern to achieve the desired thermal distribution throughout the device. The heating elements can be controlled either by an applied voltage or current. The method that is chosen depends on the application. For example in an automobile, the likely power source will be the automobile's battery. The heating elements could, therefore, be voltage controlled.

A single heating element (or temperature sensor, or cooling element) or multiple heating elements (or temperature sensors, or cooling elements) may be used to control the temperature of any given sensing electrode(s).

Heating elements (or temperature sensors, or cooling elements) may be underneath (and appropriately aligned with) an individual or multiple sensing electrode(s), separated from the sensing electrode(s) and solid electrolyte by one or more thermally insulating or thermally conducting layers.

The heating elements (or temperature sensors, or cooling elements) may be separated from each other by thermally insulating or thermally conducting layers, by the geometry of the substrate or other layers, or by empty spaces between them.

The heating elements (or temperature sensors, or cooling elements) may be suspended in cavities for thermal isolation from other regions of the device.

The heating elements (or temperature sensors, or cooling elements) may also be completely covered by thermally insulating or thermally conducting layers (i.e., embedded in the device) and may exist in any of the device layers.

Platinum may be selected for the fabrication of heating elements, temperature sensors, and/or cooling elements. Platinum is an industry standard for high-temperature resistance-temperature-devices (RTD) and as heating elements in gas sensors because of durability and chemical and thermal stability. However, other materials may be used as heaters in such devices. Also, other materials may be used for the temperature sensors or cooling elements.

Also, with the incorporation of temperature control into such devices it may be possible to reverse electrode "poisoning" or other phenomena that keep the device from responding in a repeatable way for exposure to a given gas(es) and concentration(s) which results in changes in sensor performance over time or complete failure of the device.

Embodiments of the invention can improve selectivity of more than one gas species and/or can improve the sensitivity to more than one gas species. A single device with an array of electrode-pairs can both improve sensitivity and selectivity.

The device shown in Figures 1 and 2 includes a sensor array with integrated Platinum heater and temperature sensors that were fabricated for small size and low power-consumption. The array includes two (semiconducting) La_2CuO_4 (LCO) electrodes **1, 3** and a Platinum (Pt) reference electrode **2** all on the same side of rectangular, tape-cast Yttria-Stabilized-Zirconia (YSZ) substrate **4**. In alternative embodiments, all three electrodes can be one material, such as LCO, or each electrode can be a different material. Platinum resistor elements are used as heaters **5** and/or temperature sensors **5, 6, 7** to control and monitor the temperature of the sensing electrodes. Finite Element Modeling was used to predict temperature profiles within the array. The array was then designed to keep LCO electrode **1** hotter with respect to the other two electrodes. The results from this device demonstrated that a gas sensor array with sensing electrodes kept at different temperatures can yield a device capable of selectively determining NO and NO_2 concentrations. The individual concentrations of these gases can be calculated during operation. Different sensing electrode materials and/or different temperature differentials between sensing electrodes can be used for detection of other gases and/or determination of the concentrations of other gases.

Referring to Figures 7-8, a different gas sensor array based on YSZ **12** includes two LCO sensing electrodes and two Platinum reference electrodes. The inner LCO **9** and Pt **10** electrodes are heated, while the outer LCO **11** and Pt **8** electrodes remain near the ambient temperature. Pt elements **14** and **15** are used to heat and measure temperature, while **13** and **16** are used only to measure temperature. This device offers the ability to measure the potential difference between multiple pairs of electrodes. In further embodiments, the heating elements and/or temperature sensing elements can be located on the same side of the substrate as the sensing electrodes or detached from the substrate.

From the trends with changes in specific electrode temperatures, the slopes of the plots in Figures 9-10 (and similar sensor response plots for the other electrode-pairs), which represent the sensitivity (mV change in signal per decade change in gas concentration) were used to make sensitivity plots in Figures 11-16. Each line represents a different heater setpoint, which in turn represents a separate temperature difference ($|dT|$) between the electrodes as shown. This was repeated for each of the six signals from the four sensing

electrodes. In the trend plots, the case where |dT| is zero represents measurements when the heaters were not being operated.

Figure 17A shows a contour plot for temperature variation in the sensor array of Figures 7-8 during operation. Each contour in the plot represents a given temperature within the device. A temperature profile through the middle of the device can be seen in figure 17B. Note that the sensor array of Figures 7-8 was made by hand and the results are therefore not necessarily ideal. Therefore, each of the electrodes, even when made of the same material, was slightly different from each other. When the electrode-pair is of the same material and the heater is not being operated, the sensitivity should be zero. However, as indicated in the plots the sensitivity is in fact nonzero.

Also note that the plots of Figures 9-16 are labeled to show the respective electrode-pairs, which make up six unique signals. In the plots, electrodes **8**, **9**, **10**, and **11** from Figures 7-8 are designated as Pt(1), LCO(2), Pt(3), and LCO(4), respectively. At a certain setpoint, the unheated electrodes slightly began to increase in temperature due to the specific design of this array. This can be corrected very easily with minor changes in the design such as moving the unheated electrodes further away from the heated electrodes, or creating a thermal insulation barrier. The device can be improved with changes in the heater design and layout of the electrodes with respect to the heaters and to each other. Also, the heaters can be arranged differently with respect to each other. Thermal modeling helps determine what to expect in device performance with respect to temperature uniformity.

Referring to Figures 11 and 12, showing the signals from the LCO(4)-LCO(2) and Pt(3)-Pt(1) electrode-pairs, the sensitivity of the electrode pairs is changed as the temperature difference between them increases. For LCO(4)-LCO(2), the NO sensitivity significantly increases as the temperature of the heated electrode, LCO(2), rises. In fact there is almost an increase of ten times the initial sensitivity when no temperature difference exists between the electrodes. As the heater setpoints increase, the NO_2 sensitivity decreases to almost zero. There is a slight increase in sensitivity at later setpoints, but at least over a small range of the setpoints this electrode-pair is insensitive to NO_2. Therefore this electrode-pair shows sensitivity only to NO and should be NO selective. The signals from Pt(3)-Pt(1), further demonstrate that by changing the temperature of individual electrodes of the same material, the sensitivity can be changed.

Referring to Figures 13 and 14, showing the signals from the LCO(2)-Pt(3) and LCO(4)-Pt(1) electrode-pairs, the sensitivity of the electrode pairs is changed as the

temperature difference between them increases. For LCO(2)-Pt(3), the electrode-pair effectively has become insensitive to NO. However, the NO_2 sensitivity becomes more positive and changes from a negative response to a positive response as the temperature difference between the electrodes increases. Therefore, this electrode-pair is selective to NO_2. For LCO(4)-Pt(1), the NO sensitivity remains nearly fixed at the level where the signal is without the heater in operation. This demonstrates that by changing the temperature of individual electrodes, the sensitivity can be changed for electrodes of different materials.

Referring to Figures 15 and 16, showing the signals from the LCO(4)-Pt(3) and LCO(2)-Pt(1) electrode-pairs, the sensitivity of the electrode pairs is changed as the temperature difference between them increases. For LCO(4)-Pt(3) the sensitivity to NO nearly doubles with respect to the condition without a difference in temperature between the electrodes. Also, the sensitivity to NO_2 becomes more positive and changes from a negative response to a positive response as the temperature difference between the electrodes increases. This indicates that at some temperature difference between the two electrodes, the NO_2 sensitivity should go to zero. For LCO(2)-Pt(1), the NO sensitivity becomes increasingly negative as the temperature difference between the electrodes is increased. This shows that large changes in sensitivity to both NO and NO_2 are possible by having different temperatures of electrodes making up an electrode-pair.

Figures 18 through 21 demonstrate a variety of additional sensor embodiments that are possible. Figure 18A represents a cross-section of a device similar to that shown in Figures 1 and 2 and Figures 7 and 8. In this embodiment, electrolyte layer **17** is still coupled with sensing electrodes **18** (which can be the same or different from each other). However, Pt elements **19** (used as heaters and/or temperature sensors), exist on top of support material **20**. The support may be an electric insulator or electrolyte, which may be the same or different from electrolyte layer **17**. The electrolyte **17** (and attached sensing electrodes **18**) cover the Pt elements **19** and also sit atop the support **20**. The embodiment shown in Figure 18B is similar to that shown in Figure 18A, with sensing electrodes **21** still being coupled to an electrolyte layer **22** on top of support **23**. The main difference is that the Pt elements **24** are now embedded in the support **23**. In Figure 18C, the device incorporates a support material **25** with sensing electrodes **26** and electrolyte **27** on top. The electrolyte layer **27** is in contact with support **25**. Pt elements **28** exist on the backside of support **25**. Figure 18D incorporates one electrolyte layer **29** for one (or more than one) electrode-pair made up of (same or different) sensing electrodes **30**. Another electrolyte layer **31**, also with sensing electrodes **30**,

exists separately from electrolyte **29**. Both electrolyte layers **29** and **31** exist on top of support **32**. Backside Pt elements **33** exist on the support as well. Multiple combinations of this arrangement are possible.

Figure 19 shows a cross-section of an embodiment which has (same or different) sensing electrodes **34** on one side of an electrolyte **35**, which has Pt elements **36** embedded in side. On the other side of electrolyte **36**, are additional (same or different) sensing electrodes **37**. Electrode pairs may be made up of any combination of sensing electrodes **34** and **37**. Having sensing electrodes on opposite sides of the device results in a separation of the local gaseous environment around each sensing electrode, and in certain situations will result in a reduction of cross-talk and improved selectivity.

Figure 20 is a cross-section of an embodiment which has a hollow chamber in the middle of the device. In a fashion similar to that used in the embodiment of Figure 19, this chamber acts to separate the local environment of the sensing electrodes and can be used to provide a separate gas stream of known concentration as a reference. The device incorporates (same or different) sensing electrodes **38** on the outside and (same or different) sensing electrodes **39** inside of the hollow space and attached to electrolyte **40**. Pt elements **41** may exist on the inside (or outside) of the chamber, also attached to electrolyte **40**. Additional Pt elements for heating or temperature sensing may be arranged about the device in various locations.

Figures 21A and 21B show the top view of embodiments where the electrode arrangement relative to the substrate is different from that shown in Figures 1 and 2 and Figures 7 and 8. Figure 21A shows an embodiment with (same or different) sensing electrodes **42** atop an electrolyte and/or structural support **43**. Compared to other embodiments, the sensing electrodes **42** are staggered and separated from each other on the top of the electrolyte (support) **43**. Figure 21B shows an embodiment where the sensing electrodes **44** are oriented in a different manner with respect to the electrolyte and/or support **45** and gas flow direction than the embodiment shown in Figure 21A. Various arrangements and features such as those shown in other embodiments may be used for Pt elements (used as heaters and/or temperatures sensors), other temperature sensors or cooling elements, with respect to these and other embodiments.

Figures 22 through 31 represent signals from the device in Figures 7 and 8, demonstrating that using a method and/or apparatus in accordance with embodiments of the invention, a sensor array can be made selective to a specific gas species as the temperature of

individual electrodes is changed. Again, the difference in the temperature between electrodes and the absolute temperature of each electrode is important for sensor performance. Figures 22 through 25 show the NO_x gas mixture results for the LCO(2)-Pt(1) signal, while the LCO(4)-LCO(2) signal is demonstrated in Figures 26 through 31.

Figure 22 represents the LCO(2)-Pt(1) sensor response to NO_2 gas exposure for gas mixture conditions of 0 ppm NO (solid lines) and 200 ppm NO (dashed lines). The x-axis of the plot has a log scale. The square, circle, and diamond symbols represent the conditions where 0, ~13, and ~54 mW of total power were delivered to the Pt heating elements resulting in greater temperature differences (dT) between electrodes. As can be seen, the slope of each set of lines, which represents the sensitivity (mV change in signal per decade change in gas concentration) to NO_2, increases with application of heater power. Furthermore, the sensitivity is mostly unaltered by addition of NO during NO_2 exposure. Figure 23 shows the sensor response for NO gas exposure with 0 ppm NO_2 (solid lines) and 200 ppm NO_2 (dashed lines). The x-axis of the plot has a log scale. As seen in Figure 23, the sensitivity to NO decreases as the power to the heaters increases. Also marked in this figure for each heater setpoint are the approximate shifts in NO sensitivity when 200 ppm NO_2 is added to the gas mixture. The shifts are all negative as expected when considering the larger (negative) response to NO_2 as shown in Figure 22. As the heater power increases, the shift becomes more uniform over the entire range of NO concentrations probed. At lower heater power, the shift is more prominent for higher NO concentrations (i.e., the sensitivity decreases with addition of 200 ppm NO_2). Without the use of the heaters, the shift in the sensor response is 0.18 to 1.3 mV along the entire NO concentration range. For 13 mW of heater power, the shift is between 3.2 and 3.7 mW. At 54 mW, the heater power is sufficient to reduce the NO response to such a degree that the curve is horizontal. When 200 ppm NO_2 is introduced, the curve remains horizontal but shifts to more negative values by 6.8 mV.

Figure 24 shows the NO_2 sensor response with the same conditions as Figure 22 for 0 ppm NO. However, the x-axis has a linear scale and this plot includes data points for the condition of 0 ppm NO_2. Also marked in Figure 24, are the difference in the measured voltage difference between the 0 ppm NO_2 baseline and the 200 ppm NO_2 gas step. When the results for NO (0 ppm and 200 ppm NO_2) in Figure 23 are compared to the changes in voltage between the 0 ppm NO_2 baseline and 200 ppm NO_2 gas step (Figure 24), the improvements in NO_2 selectivity with increasing heater power are clear. Without the use of the heaters, a change from 0 ppm to 200 ppm NO_2 produces a change in voltage of 3.5 mV

(Figure 24), while there is a shift of 0.18 to 1.3 mV between these two conditions when NO is also present in the gas mixture (Figure 23). This difference can be debilitating when trying to determine NO and/or NO_2 gas concentrations in a gas mixture because the actual voltage measured is different from that which is expected. When a small amount of power is delivered to the heaters (~13 mW), the situation improves slightly as evidenced when comparing the expected change in voltage of 5 mV (Figure 24) to the actual change of 3.2 to 3.7 mV seen when NO and NO_2 are present (Figure 23). As mentioned previously, a heater setpoint delivering 54 mW of power results in increased NO_2 sensitivity (Figure 22) and a complete removal of NO sensitivity (horizontal curve in Figure 23). Furthermore, the expected voltage change between conditions of 0 ppm and 200 ppm NO_2 is 6.5 mV (Figure 24). This is almost exactly the same as the shift (6.8 mV) during NO gas exposure when measurements are also made in the presence of 0 ppm and 200 ppm NO_2. Now that gas mixtures of NO and NO_2 do not affect the expected voltage change to variations in NO_2, the gas sensor array can be used to accurately portray the real concentration of NO_2 gas present in the gas mixture. Using the same principles, the sensor array can be made to have improved selectivity to any gas, such as NO, NO_2, NH_3, CO, CO_2, and/or hydrocarbons.

Figure 25 shows a plot of sensitivity versus total heater power for the LCO(2)-Pt(1) signal of the embodiment in Figures 7 and 8 with gas mixture conditions of NO (0 and 200 ppm NO_2) and NO_2 (0 and 200 ppm NO), as indicated. The sensitivity to NO, with and without the presence of NO_2, decreases to 0 mV/decade ppm NO as the heater power increases. As this happens, there is also a decrease in the change in sensitivity seen when 200 ppm NO_2 is introduced into the gas mixture. The sensitivity to NO, with and without the presence of NO_2, decreases to 0 mV/decade ppm NO as the heater power increases. As the heater power increases, the sensitivity to NO_2, with and without the presence of NO, almost increases by a factor of 2. The sensitivity to NO_2 with 0 ppm and 200 ppm NO, remains mostly unchanged over the same range of heater power. Moreover, by operating this electrode pair at the maximum dT (obtained with 54 mW of heater power) a sensor is obtained that has both higher sensitivity and selectivity to NO_2, since the cross sensitivity to NO is removed (becomes zero or negative).When considering these changes in sensitivity and the voltage shifts observed with exposure of gas mixtures of NO and NO_2 as mentioned earlier, it is clear that the overall sensor array performance can be enhanced using embodiments of the subject method.

Figures 26 through 28 show how the LCO(4)-LCO(2) electrode-pair, of the embodiment of Figures 7 and 8, can be used to detect total NO_x concentrations when NO and NO_2 exist in a gas mixture together. The LCO(4)-LCO(2) response to NO_2 gas exposure for gas mixture conditions of 0 ppm NO (solid lines) and 200 ppm NO (dashed lines) is shown in Figure 26 for total heater power of 0, 13, and 54 mW as indicated. For the same total heater power, Figure 27 shows the response to NO gas exposure for gas mixture conditions of 0 ppm NO_2 (solid lines) and 200 ppm NO_2 (dashed lines) . Referring to Figures 26 and 27, the response to NO_2 (0 and 200 ppm NO) gas mixtures always shows a positive response. The same is true for NO (0 and 200 ppm NO_2) gas mixtures and except for the case when the heaters are not used (0 mW total heater power), where there is essentially no sensitivity to NO. Furthermore, the shift in the LCO(4)-LCO(2) signal is always positive when NO is introduced to NO_2 gas steps, as in Figure 26, and when NO_2 is added to NO gas steps, as in Figure 27. When there is a shift in response for both the case in Figure 26 and 27, the slope remains relatively unchanged, even at the higher total heater power setting. This is shown in Figure 28, which is a plot of sensitivity (mV/decade ppm NO or NO_2) versus total heater power for NO (0 and 200 ppm NO_2) and NO_2 (0 and 200 ppm NO), as indicated. Also note in this figure, that the sensitivity to both NO and NO_2 increases with increasing total heater power as the temperature of the LCO(2) electrode increases. A unique voltage difference is produced for each combination of NO and NO_2 concentrations. This is demonstrated in Figures 29 through 31, which show the sensor response versus total ppm NO_x in the gas mixture for 0 mW, 13 mW, and 54 mW respectively. In the case where the heaters are not used (Figure 29), the LCO(4)-LCO(2) signal is insensitive to NO but has sensitivity to NO_2. Therefore, under these conditions the LCO(4)-LCO(2) electrode-pair is selective to NO_2. However, as evident from Figures 29 through 31, as the temperature of the heated LCO(2) electrode increases (i.e., when the heater power is applied), the total NO_x measurement becomes possible as the signal begins to become sensitive to NO, while remaining sensitive to NO_2. Comparing Figures 30 and 31, as the heater power is increased further, the sensitivity to NO and NO_2 increases even more. Furthermore, there is overlap between the gas mixture measurements involving NO (0 and 200 ppm NO_2) and NO_2 (0 and 200 ppm NO). For example, at a total NO_x concentration of 400 ppm (200 ppm NO and 200 ppm NO_2), the sensor response is exactly the same regardless of whether the measurement was made in dynamic gas steps of NO_2 with static NO concentration, or vice versa. In summary, by changing the temperature of at least one sensing electrode with respect to another, it becomes

possible to measure the total NO_x in gas mixtures of NO and NO_2 even when using the same materials for each electrode making up the electrode-pair.

As demonstrated in Figures 22 through 31, the embodiment in Figures 7 and 8 and similar sensor arrays have the capability of detecting the individual concentrations of NO and NO_2. This is possible because the LCO(2)-Pt(1) electrode-pair can selectively detect NO_2 over NO in NO_x gas mixtures when the LCO(2) electrode is heated locally. Furthermore, the LCO(4)-LCO(2) electrode-pair, which is made up of two sensing electrodes of the same material but different temperatures, is able to detect total NO_x. The concentration of NO can be calculated by subtracting the detected NO_2 concentration from the detected NO_x concentration. Though this method is indirect, it is possible that using the same method of locally heating individual electrodes making up electrode-pairs of similar or different temperatures that an electrode-pair(s) can provide selective detection of NO, NO_2, (or CO, CO_2, ammonia, and other gases) as demonstrated in Figures 9 through 16.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows a specific embodiment of a device in accordance with the subject invention.

Figure 2 shows a cross-sectional view of the embodiment of Figure 1.

Figure 3 shows the sensor response vs. concentrations of NO_2 for the non-heated LCO electrode vs. the non-heated platinum electrode taken from the three sensing electrodes.

Figure 4 shows the sensor response vs. concentrations of NO_2 for the heated LCO electrode vs. the non-heated platinum electrode taken from the three sensing electrodes.

Figure 5 shows the sensor response vs. concentrations of NO_2 for the heated LCO electrode vs. the non-heated platinum electrode taken from the three sensing electrodes.

Figure 6 shows the sensor response vs. concentrations of NO_2 for the non-heated LCO electrode vs. the non-heated platinum electrode taken from the three sensing electrodes.

Figure 7 shows an additional embodiment of the subject invention.

Figure 8 shows a cross-sectional view of the embodiment in Figure 7.

Figure 9 shows the sensor response vs. concentrations of NO for the electrode pair having the non-heated LCO sensing electrode and the heated platinum sensing electrode, LCO(4)-Pt(3), showing the results for increasing temperatures difference.

Figure 10 shows the sensor response vs. concentrations of NO_2 for the electrode pair having the non-heated LCO sensing electrode and the heated platinum sensing electrode, LCO(4)-Pt(3), showing the results for increasing temperatures.

Figure 11 shows the signal results from the LCO(4)-LCO(2) and Pt(3)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO.

Figure 12 shows the signal results from the LCO(4)-LCO(2) and Pt(3)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO_2.

Figure 13 shows the signal results from the LCO(2)-Pt(3) and LCO(4)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO.

Figure 14 shows the signal results from the LCO(2)-Pt(3) and LCO(4)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO_2.

Figure 15 shows the signal results from the LCO(4)-Pt(3) and LCO(2)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO.

Figure 16 shows the signal results from the LCO(4)-Pt(3) and LCO(2)-Pt(1) electrode-pairs, of the embodiment in Figures 7 and 8, in response to changes in gas concentration of NO_2.

Figure 17A shows the temperature contour plot for embodiment shown in Figures 7 and 8.

Figure 17B shows the temperature profile through the cross-section of Figure 17A.

Figure 18A shows an embodiment with structural support and electrolyte with embedded heaters and sensing electrodes deposited on top, where a multitude of electrode pairs may exist.

Figure 18B shows an embodiment with structural support with embedded heaters and electrolyte and sensing electrodes deposited on top, where a multitude of electrode pairs may exist.

Figure 18C shows an embodiment with structural support with backside heaters and topside deposited electrolyte and sensing electrodes, where a multitude of electrode pairs may exist.

Figure 18D shows an embodiment with structural support with backside heaters and separate electrolyte layers with sensing electrodes for different electrode-pairs, where a multitude of electrode pairs and electrolyte layers may exist.

Figure 19 shows an embodiment with an electrolyte support with embedded heaters, and sensing electrodes on opposite sides of the electrolyte, where a multitude of electrode pairs and electrolyte layers may exist.

Figure 20 shows an embodiment with one or more chambers inside the structural electrolyte, with heaters deposited on one side of the chamber, sensing electrodes are positioned on the other side, and additional sensing electrodes positioned on the outside of the structural electrolyte, where the chamber can be used for a reference gas.

Figure 21A shows an embodiment with sensing electrodes staggered and separated from each other on the top of the electrolyte and/or structural support.

Figure 21B shows an embodiment the sensing electrodes oriented in a different manner with respect to the gas flow direction.

Figure 22 shows a (log scale) plot of the sensor response to NO_2 for the LCO(2)-Pt(1) electrode-pair of the embodiment in Figures 7 and 8, tested at a higher ambient temperature than for Figures 9 to 16, for several different instances of total heater power, where conditions tested include gas steps of NO_2 with 0 ppm NO and 200 ppm NO gas mixtures.

Figure 23 shows a (log scale) plot of the sensor response to NO for the LCO(2)-Pt(1) electrode-pair of the embodiment in Figures 7 and 8, tested at a higher ambient temperature than for Figures 9 to 16, for several different instances of total heater power, where conditions tested include gas steps of NO with 0 ppm NO and 200 ppm NO_2 gas mixtures, where the shifts in response caused by introduction of NO_2 into the NO gas stream are also marked.

Figure 24 shows a (linear scale) plot of Figure 22, for the embodiment in Figures 7 and 8, with the voltage change from 0 to 200 ppm NO_2 marked for each heater power condition.

Figure 25 shows sensitivity versus total heater power for the LCO(2)-Pt(1) electrode-pair, for the embodiment in Figures 7 and 8, taken from Figures 22 and 23.

Figure 26 shows the NO response of the LCO(4)-LCO(2) electrode-pair of the embodiment in Figures 7 and 8, tested at a higher ambient temperature than for Figures 9 to 16, for several different instances of total heater power.

Figure 27 shows the NO_2 response of the LCO(4)-LCO(2) electrode-pair of the embodiment in Figures 7 and 8, tested at a higher ambient temperature than for Figures 9 to 16, for several different instances of total heater power.

Figure 28 shows the sensitivity versus total heater power for the LCO(4)-LCO(2) electrode-pair, for the embodiment in Figures 7 and 8, taken from Figures 26 and 27.

Figure 29 demonstrates the total NO_x sensing capability of the LCO(4)-LCO(2) electrode-pair, for the embodiment in Figures 7 and 8, without the use of the heaters (i.e., total heater power is 0 mW).

Figure 30 demonstrates the total NO_x sensing capability of the LCO(4)-LCO(2) electrode-pair, for the embodiment in Figures 7 and 8, for a total heater power of 13 mW.

Figure 31 demonstrates the total NO_x sensing capability of the LCO(4)-LCO(2) electrode-pair, for the embodiment in Figures 7 and 8, for a total heater power of 54 mW.

DETAILED DISCLOSURE

Embodiments of the subject invention relate to a gas sensor and method for sensing on or more gases specific embodiments pertain to a potentiometric gas sensor and method for sensing on or more gases. Additional embodiments are directed to amperometric and/or impedimetric gas sensors and method for sensing one or more gases. An embodiment incorporates an array of sensing electrodes maintained at similar or different temperatures, such that the sensitivity and species selectivity of the device can be fine tuned between different pairs of sensing electrodes. A specific embodiment pertains to a gas sensor array for monitoring combustion exhausts and/or reaction byproducts. An embodiment of the subject device related to this invention operates at high temperatures and can withstand harsh chemical environments.

Embodiments of the device can have sensing electrodes in the same environment, which allows the electrodes to be coplanar. The sensitivity and selectivity of these sensors can vary with temperature. Therefore, with respect to specific embodiments, the temperature of the device can be precisely controlled and can be changed rapidly when desired. In order to achieve a device that is able to monitor two or more gas species of interest, an array of sensing electrodes can be incorporated. The array signals can then be entered into linear algorithms (or other appropriate algorithm(s)) to determine the presence of and/or concentrations of one or more individual species. As pattern recognition is not an easy task to accomplish and may require additional electronics, thereby driving up the cost of the

device, it may be preferred to have the capability of individually monitoring a single species in the presence of others, with minimal interference. In this way, the device will not require extensive pattern recognition, if any at all.

Embodiments of the invention can provide improvements in selectivity and sensitivity via thermal modification of individual sensing electrodes and/or the entire device. Furthermore, improvements in signal noise can be achieved if the temperature is uniformly maintained. Also, with the incorporation of temperature control into embodiments of the subject device, it is possible to reduce or reverse electrode "poisoning" or other phenomena that results in changes in sensor performance over time or complete failure of the device.

The subject method and device can be used for the monitoring of combustion byproducts or other processes for chemical/gas monitoring. In a specific embodiment, the device can be used to monitor the exhausts in automobiles to determine if the catalytic converter has malfunctioned or to provide information for adjusting the air-to-fuel ratio in the engine based on EPA (or other) requirements, which will change as driving conditions differ. The subject device may also be used to monitor combustion byproducts (or other chemical/gas related processes) at a power plant or any industrial manufacturing processes.

An embodiment of a sensor array in accordance with the invention incorporates an integrated Platinum heater and temperature sensors fabricated for small size and low power-consumption. The array includes two La_2CuO_4 electrodes and a Platinum reference electrode all on the same side of a rectangular, tape-cast YSZ substrate. Platinum resistor elements are used as heaters and/or temperature sensors to control and monitor the temperature of the sensing electrodes. Finite Element Modeling was used to predict temperature profiles within the array. The array was then designed to keep one La_2CuO_4 electrode hot with respect to the other two electrodes. The results of from this device demonstrated that a gas sensor array with sensing electrodes kept at different temperatures can yield a device capable of selectively determining NO and NO_2 concentrations. In additional embodiments, the selectivity of a sensor array can be enhanced through control of the local temperature of the sensing electrodes.

Control of the local temperature of the sensing electrodes can be implemented by cooling in addition to or instead of heating. Passive and/or active cooling techniques known in the art can be incorporated with the subject invention.

Sensing electrodes can be made from metals (e.g., Platinum), semiconductors (e.g. semiconducting oxides such as La_2CuO_4 or WO_3), or other material showing sensitivity to a

gas. In general, any given sensing electrode material will have varying sensitivity and selectivity to different gas species depending on the temperature of the electrode. The degree to which sensitivity and/or selectivity that changes depends on the material, gas, and temperature. Each electrode may be part of one or more "electrode-pairs". This means that the measurable number of signals can be larger than the actual number of sensing electrodes. Specifically, the design of the sensor array can include (either as individual devices or together in a single device) two different "electrode-pair" schemes. One scheme can use multiple materials at the same time, which may be kept at the same and/or different temperature. The control of the temperature can be accomplished via heating and/or cooling techniques. A device may also incorporate multiple electrodes of the same material that are maintained at one or more different temperatures. Electrodes of the same material may be kept at the same temperature, one or more other features of the electrodes, such as microstructure, size, or thickness, can be different for different electrodes. Accordingly, the gas sensor arrays may utilize one or more of these schemes in a single device, depending on the application.

Gas sensors in accordance with the invention can incorporate specifically designed heating elements to control the temperature topside of individual sensing electrodes. In an embodiment, the sensing electrodes are on topside of, and the heating elements are on the backside, of a substrate. In another embodiment, the sensing electrodes are on both sides of the substrate. The substrate can be, for example, a YSZ substrate or other electrolyte. The substrate may also be a structural support, such as Al_2O_3, with an electrolyte layer on top. The heating elements can be made of any material, such as platinum, that has the thermal and chemical stability to not degrade with time in a harsh environment. The heating elements can act as resistors and produce heat via Joule heating, by passing electrical current through the heating elements.

In accordance with various embodiments of the subject invention, a variety of electrolyte materials for the substrate can be used and a variety of materials can be used for the sensing electrode and any heating elements can be used. Examples of suitable materials are taught in U.S. 6,598,596, which is incorporated herein by reference in its entirety. The electrodes can be made from a variety of materials, including metals, and semiconductors. The semiconductor material is preferably a metal oxide or a metal oxide compound. The terms ""metal oxide" and ""metal oxide compound" are used interchangeably herein to mean a compound having elemental metal combined with O2. Examples of metal oxides that are

useful in the invention include SnO2, TiO2, TYPd5, MoO 3, ZnMoO4 (ZM) and WO3 and WR3, La2CuO4, and mixtures thereof. The semiconductor materials can include a metal oxide. The metal oxide is preferably SnO2, TiO2, TYPd5, MoO3, ZnMoO4 or WR3, where TYPd5 and WR3 are acronyms defined below. The acronym TYPd5 is used herein to represent a composite prepared by selecting TiO 2 (titania), Y2O3 yttria) and Pd in a weight ratio of approximately 85:10:5.

The electrolyte is preferably an oxygen ion-conducting electrolyte. The oxygen ion-conducting electrolyte can be based on ZrO2, Bi2O3 or CeO2. Preferred oxygen ion-conducting electrolytes are electrolyte mixtures, the mixtures generally including a base material, such as ZrO2, Bi 2O3 or CeO2 and one or more dopants, such as calcia (CaO) and yttria (Y2O3) which can function as stabilizers, or some other suitable oxygen ion-permeable material. For example, yttria stabilized zirconia (YSZ) electrolytes can be formed by mixing yttria and ZrO2. Electrolytes that conduct ionic species other than oxygen ions, e.g., halides, are well known in the art and also find utility in the invention for measuring halogen-containing gas species. The choice of material for electrolyte can depend on the component in the gas mixture to be measured. Thus, to measure the concentration of an oxide component, for example, NOx, COx or SOx the electrolyte is preferably an oxygen-ion conducting electrolyte. Preferred oxygen ion-conducting electrolytes are electrolyte mixtures based on zirconia (ZrO 2), bismuth oxide (Bi2 O3), and ceria (CeO 2). Practical electrolyte mixtures generally include one or more dopants, such as calcia (CaO) and yttria (Y2O3), or some other suitable oxygen ion-permeable material.

A specific embodiment of a gas sensor array includes two LCO sensing electrodes and two Platinum reference electrodes. The inner LCO and Pt electrodes are heated, while the outer LCO and Pt electrodes remain near the ambient temperature. Furthermore, the potential difference between multiple pairs of electrodes can be measured in order to provide signals. Since no two electrodes have the same combination of material and operating temperature, there are a total of six distinct signals that can be measured by pairing the four electrodes. These signals can be compared to help determine the gas concentrations in a mixture of gases.

The temperature control of these devices can be important. Precise control of temperature with minimal fluctuations can allow the device to produce stable sensor signals. Therefore, thermal modeling can be performed during the design phase to provide

information regarding the temperature profile in the device for different locations of the sensing electrodes and the heating electrodes on the substrate of the array.

Platinum can be used for the fabrication of heating elements and temperature sensors. Platinum is an industry standard for high-temperature resistance-temperature-devices (RTD) and as heating elements in gas sensors because of durability and chemical and thermal stability. However, other materials may be used as heaters in the subject devices.

Surface temperature measurements can be difficult and some of the best methods available include use of optical infrared sensors and RTDs. Below approximately 400 °C the resistance of Platinum has a linear dependence on temperature. However, above this temperature, further heat loss causes the linear model to deviate from experimental data, and an alternative model is

$$R(T) = a\left(1 + bT - cT^2\right) \qquad (1)$$

where a, b, and c are empirical coefficients. After the data is fit to the model, software can calculate the surface temperature during sensor operation using the coefficients from (1) and resistance measurements of the Platinum elements.

Heating elements can be used not only to heat another object but also simultaneously as a temperature sensor. If the resistance of the heater can accurately be determined (e.g., using a four-wire method), then the temperature of the Platinum element can be calculated. Resistance increases as current is supplied to the heater because of Joule heating. This does not greatly affect the voltage or current measurements. That is to say, the measurements represent the actual current in the circuit and voltage drop across the heater. Therefore the calculated resistance, and hence temperature, of the heater represents the real value.

The heating element shape is important to the temperature distribution. In an embodiment, the temperature of the sensing electrode is uniform, or, if desired, nonuniform in a preferred manner. In an embodiment, the heating elements are C-shaped. Serpentine-patterned heaters can also be utilized. Spiral shaped heaters, or any other shaped heaters, can also be used. The heating elements can be controlled either by an applied voltage or current. The method of controlling the heating elements utilized depends on the application. As an example, in an automobile, the automobile's battery can be the power source, such that the heating elements would be voltage controlled.

In a specific embodiment, a YSZ substrate can have multiple sensing electrodes on one side. Platinum (or other resistive material) elements are on the opposite side of the YSZ

substrate, aligned with the electrodes. The sensing electrodes may also be oriented in a symmetric or nonsymmetrical fashion with respect to each other, and they may be staggered. The Platinum (or other resistive material) elements need not be used as heaters. The Platinum elements may be used as heaters and/or temperature sensors. In another embodiment, the semiconductive elements can be used for cooling of the electrodes via, for example, thermoelectric cooling. The cooling elements may also be made of any material which allows cooling of specific regions in the device. The thermal characteristics of the heating/cooling elements and/or surface temperature sensors can be improved with the use of insulating materials integrated into the device structure or by other specific shape or design change to the device that impacts the thermal properties of the device, such as empty volumes. The shape of the substrate can also vary.

Figure 1 shows a specific embodiment of a device in accordance with the subject invention, and Figure 2 shows a cross-sectional view of the same embodiment. The device includes two La_2CuO_4 electrodes with a Platinum electrode in between, on a first side of a substrate, where the substrate is an electrolyte. A Platinum heater and two Platinum temperature sensing elements can be positioned on the other side of the substrate. Figures 3-6 show the sensor response vs. concentrations of NO and NO_2 for two different electrode-pair combinations taken from the three sensing electrodes. These results show that the device was able to produce a signal that was mainly sensitive to NO_2 and a signal that was sensitive to both NO and NO_2. Thus, indirect detection of individual concentrations of NO and NO_2 is possible via substraction.

Figure 7 shows another specific embodiment of the subject invention, and Figure 8 shows a cross-sectional view of the same embodiment. The device includes two La_2CuO_4 electrodes and two Platinum electrodes, interdigitated with each other, on one side of a substrate. On the other side of the substrate, incorporating an electrolyte, are four Platinum electrodes, where the inner two are heaters and temperature sensors and the outer two are temperature sensors. This arrangement allows the two LCO electrodes to be maintained at different temperatures and the two Platinum sensing electrodes to be at different temperatures. If the two heated electrodes are maintained at constant temperatures, this allows six electrode-pair combinations for receiving signals. If the heated electrodes are designed to have more temperatures during operation, then more electrode-pair combinations can be created, with a specific electrode at two different temperatures acting as two electrodes for the purposes of providing output sensor signals. Figures 9-10 show sensor responses for

NO and NO_2 for the electrode-pair having the non-heated LCO electrode and the heated Platinum electrode showing the results for increasing temperature difference and absolute temperature of each electrode. The slopes of the plots from Figures 9-10 can be taken, which represent the sensitivity (mV change in signal per decade change in gas concentration), to make trend plots provided in Figures 11-16. Each curve represents a different heater setpoint, which in turn represents a different temperature difference between the electrodes for the device shown in Figures 7-8. This was repeated for each of the six electrode signals from the four sensing electrodes for the device shown in Figures 7-8. In the trend plots the curve where |dT| is equal to zero is the case where the heaters were not being operated.

With respect to the device shown in Figures 7-8, more sensor signals can be measured than the number of sensing electrodes on the device itself. This is possible because some of the electrodes are at different temperatures. Furthermore, the device can have electrode-pairs that are selective to NO only and other electrode-pairs that are selective to NO_2 only. Other embodiments can have electrode pairs that are selective to other gases such as CO and CO_2. In fact, for some of the heater setpoints there were examples of the electrode-pairs switching their signal direction as they went either more positive or negative. This indicates that for a given electrode material or pair of materials, if the temperature is kept different between them, then the electrode-pair can be utilized in a way that results in it being sensitive or insensitive to one or more gases.

Furthermore, the sensors can take advantage of both changes in absolute temperature and differences in temperature between electrodes making up electrode-pairs. Sensitivity to a given species typically is altered at higher temperatures. If two sensing electrodes are brought above the temperature where they are no longer sensitive to one gas, but both are still sensitive to another gas, then the signal will be selective. Additionally, it is possible that if the temperature of one of the two electrodes is further increased that the signal, which is now selective, will also benefit from an increase in sensitivity as the individual potentials of the electrodes is further changed. This can be taken advantage of based on how the sensing electrodes' sensitivity changes with temperature and the specific gas species the electrodes are exposed to. In specific embodiments, pattern recognition is not used, thereby reducing device costs and improving sensor performance. The performance is also improved because one is able to increase the sensitivity of some of the electrode-pairs using the same methods for achieving differences in temperature between the electrodes. This can also be done by changes in microstructure and geometry of device.

The array of sensing electrodes used for various embodiments of the invention can include several different sensing electrodes. A reference or pseudo-reference electrode can be included, if desired. In embodiments, each sensing electrode can be used to make up a "sensing electrode-pair." Furthermore, each sensing electrode can be used in combination with other sensing electrodes in the array to make up multiple electrode-pairs. Different electrode configurations or properties will change the way in which the sensor performs. This allows specific tailoring of the device to achieve the desired performance (e.g., sensitivity, selectivity, and response time) for specific applications.

Depending on the specific design and/or application, the sensing electrodes can be configured using the same or different electrode materials, using the same and/or different microstructures, using the same and/or different geometries (shape and thickness), and/or being operated at the same and/or different temperatures. The key is that the two electrodes to be used to create a sensing electrode-pair, when an electrolyte is in contact with the two electrodes, should create a voltage potential across the sensing electrode-pair when exposed to a gas species to be measured or to a mixture of gases which includes a gas species to be measured. By having the two electrodes have some combination of different microstructures, different geometries (shape and thickness), different materials, being at different temperatures, and/or any other alteration which causes the materials to differ in some way, the conditions to create a sensing electrode-pair can exist.

Temperature control of the sensing electrodes can be used to achieve the desired performance. Depending on the sensing electrode-pair, the performance of the measured signal can generally be modified via thermal modification. Furthermore, the temperature is preferably kept from changing due to external sources (such as changes in the gas stream temperature). Therefore, embodiments of the device can incorporate a means to monitor the temperature of the sensing electrodes and a means to change their temperatures when needed.

Heating elements can be utilized to modify the temperature of the sensing electrodes when needed. The heating elements can be on the opposite side of a substrate from the sensing electrodes, each appropriately aligned with a specific sensing electrode. Heating elements can be located on the same side of the substrate as the sensing electrodes as well. Heating elements may also be embedded in or on the electrolyte or support. Different heating element patterns can be implemented (e.g., C-shaped, spiral, or serpentine patterns) in order to yield the ideal thermal distribution on the device. The heat can be generated by Joule heating (Heat=Power*Time=Current^2*Resistance*Time). The heating current may be

voltage or current controlled and delivered in pulses or in a constant manner. The heating current may be delivered by simple current splitting or by individual (current or voltage) output to the heating elements.

The temperature of the sensing electrodes can also be controlled via cooling, either in conjunction with heating or alone. In an embodiment, cooling can be accomplished using a method known as thermoelectric cooling, for example, using a solid-state heat pump. Cooling can also be accomplished with the use of heat sinks. By changing the temperature on other areas of the device, a temperature under a sensing electrode may also be lowered. Other designs to accomplish cooling of specific regions of the device are also possible.

Temperature monitoring can be accomplished by measuring the resistance or other temperature related parameter of elements made of metal, semiconductor, or other material that cover an area under or near the sensing electrodes. Temperature sensors also may be embedded or lay exposed on the surface. Multiple methods of temperature sensing are possible including use of RTDs and thermocouples. Temperature sensors may act simultaneously as heating elements or may be stand alone elements. Temperature sensors may act simultaneously as cooling or heating elements as well.

There are several different signals that may be monitored. Some of the various signals that can be monitored include the voltage of sensing electrodes and/or voltage differences of sensing electrode-pairs. Multiplexing can be used to monitor the multiple voltage signals from the corresponding multiple sensing electrode-pairs. Resistance or other parameter monitoring of temperature sensors can also be accomplished and can also utilize multiplexing.

Various embodiments incorporate a detector for measuring an electrical characteristic with respect to the sensing electrode. One method of detection in the sensor array may be potentiometric. The array may include other methods of detection such as conductimetric (or impedancemetric), capacitve, or other methods for detecting gas species. This extension of the sensor array can be achieved monolithically or on separate substrates connected to a common measurement system.

There are numerous techniques that can be employed in the manufacture of embodiments of the subject devices. Multiple devices may be made simultaneously and separated by various means after manufacture. Any combination of the following techniques can be utilized. Multilayer fabrication, such as tape-casting, and/or screen-printing, can be used. Bottom-Up (additive) approach, such as direct-write methods (e.g., pump- or aerosol-

based deposition), laser micromachining, and/or laser sintering, can be used. Multi-step (subtractive) approach, such as microfabrication using photolithography and other techniques used in the fabrication of microelectronics and microelectro-mechanical systems (MEMS), and/or electron-beam and laser-based subtractive fabrication, can be used. Wire attachment methods and metallization, such as metals used for metallization or wire attachment must be able to withstand harsh environments. Wire bonding (e.g., Au or Pt wire), brazing, and/or other methods of wire attachment can be used. Different metallization (materials or otherwise) may exist in multiple layers and connected to each other by vias that exist in between layers or on the outside of the device. Device packaging can be accomplished via standard or other packaging techniques. Designs of high-temperature (or any other) electronics and/or sensors may be used with this device. These may be incorporated into the sensor for a monolithic device or exist as a part of a hybrid system.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

CLAIMS

What is claimed is:

1. A gas sensor, comprising:

a sensing electrode in contact with an electrolyte, wherein the electrode is exposed to an environment of interest;

a mechanism capable of altering the temperature of the sensing electrode; and

a detector for measuring an electrical characteristic with respect to the sensing electrode, wherein the measured electrical characteristic provides information with respect to one or more gases in the environment of interest.

2. The gas sensor according to claim 1, wherein the sensing electrode is disposed on a surface of a substrate, wherein the substrate comprises the electrolyte.

3. The gas sensor according to claim 1, wherein the detector measures an EMF between the sensing electrode and a reference.

4. The gas sensor according to claim 1, wherein the detector measures the impedance of the electrode.

5. The gas sensor according to claim 1, wherein the detector measures a current in the electrode.

6. The gas sensor according to claim 3, wherein the measured EMF indicates whether a first gas is present in the environment of interest.

7. The gas sensor according to claim 3, wherein the measured EMF indicates a concentration of a first gas present in the environment of interest.

8. The gas sensor according to claim 1, further comprising:

at least one additional sensing electrode.

9. The gas sensor according to claim 8, wherein one of the at least one additional electrode is the reference.

10. The gas sensor according to claim 1, wherein the mechanism capable of altering the temperature of the sensing electrode comprises a heater.

11. The gas sensor according to claim 10, wherein the heater is in thermal contact with the electrolyte.

12. The gas sensor according to claim 10, wherein the heater is detached from the electrolyte and sensing electrode.

13. The gas sensor according to claim 10, wherein the heater radiatively heats the sensing electrode.

14. The gas sensor according to claim 10, wherein the heater conductively heats the sensing electrode.

15. The gas sensor according to claim 1, wherein the heater comprises the sensing electrode and a current source for driving the electrode with a current.

16. The gas sensor according to claim 1, wherein the mechanism capable of altering the temperature of the sensing electrode is capable of cooling the sensing electrode.

17. The gas sensor according to claim 10, wherein the heater comprises a heating element, wherein when a heating current is passed through the heating element the heating element produces heat that heats the electrode.

18. The gas sensor according to claim 3, further comprising at least one additional sensing electrode in contact with the electrolyte, wherein the sensing electrode and the at least one additional sensing electrode form an array of sensing electrodes.

19. The gas sensor according to claim 18, wherein the reference is one of the at least one additional sensing electrode, wherein the reference has a different shape than the sensing electrode.

20. The gas sensor according to claim 18, wherein the reference is one of the at least one additional sensing electrode, wherein the reference is at a different temperature than the sensing electrode.

21. The gas sensor according to claim 18, wherein the reference is one of the at least one additional sensing electrode, wherein the reference is made of a different material than the sensing electrode.

22. The gas sensor according to claim 18, wherein the reference is one of the at least one additional sensing electrode, wherein the reference comprises a different microstructure than the sensing electrode.

23. The gas sensor according to claim 18, wherein upon exposure to a gas to be measured, an EMF occurs between a selected two electrodes of the array of electrodes.

24. The gas sensor according to claim 18, wherein the array of electrodes comprises electrodes formed of only the same material, wherein electrodes of the array of electrodes are maintained at one or more different temperatures by the corresponding array of heating elements.

25. The gas sensor according to claim 24, wherein any two electrodes of the array of electrodes maintained at a different temperature function as an electrode-pair.

26. The gas sensor according to claim 24, wherein the electrodes formed of the same material and maintained at a same temperature comprise one or more electrodes having different microstructures, sizes, or thicknesses.

27. The gas sensor according to claim 26, wherein any two electrodes of the array of electrodes maintained at a different temperature, having a different microstructure, having a different size, and/or having a different thickness function as an electrode-pair.

28. The gas sensor according to claim 18, wherein the array of electrodes comprises one or more electrodes of a first material and one or more electrodes of a second material, wherein the electrodes of the array of electrodes are maintained at one or more different temperatures by an array of heating elements.

29. The gas sensor according to claim 28, wherein any two electrodes of the array of electrodes formed of a different material and/or maintained at a different temperature function as an electrode-pair.

30. The gas sensor according to claim 28, wherein the electrodes formed of a same material and maintained at a same temperature comprise one or more electrodes having different microstructures, sizes, or thicknesses.

31. The gas sensor according to claim 30, wherein any two electrodes of the array of electrodes formed of a different material, maintained at a different temperature, having a different microstructure, having a different size, and/or having a different thickness function as an electrode-pair.

32. The gas sensor according to claim 18, wherein electrodes of the array of electrodes comprise metal or a semiconducting oxide.

33. The gas sensor according to claim 18, wherein electrodes of the array of electrodes comprise at least one platinum electrode.

34. The gas sensor according to claim 18, wherein electrodes of the array of electrodes comprise at least one La_2CuO_4 (LCO) electrode.

35. The gas sensor according to claim 28, wherein the array of heating elements comprise resistor elements.

36. The gas sensor according to claim 35, wherein the resistor elements are formed of platinum.

37. The gas sensor according to claim 35, wherein each resistor element is disposed in a pattern on the opposite surface of the electrolyte to one of the electrodes of the array of electrodes.

38. The gas sensor according to claim 35, wherein the pattern of each resistor element comprises a C-shape pattern, a spiral pattern, or a serpentine pattern.

39. The gas sensor according to claim 1, further comprising:
a temperature sensor for measuring the temperature of the sensing electrode.

40. The gas sensor according to claim 1, wherein the sensing electrode is made of a semiconductor.

41. The gas sensor according to claim 1, wherein the sensing electrode is made of a metal.

42. The gas sensor according to claim 1, wherein the semiconductor is a metal oxide or metal oxide compound.

43. The gas sensor according to claim 42, wherein the semiconductor comprises one or more of the following: SnO2, TiO2, TYPd5, MoO 3, ZnMoO4 (ZM) and WO3 and WR3, La2CuO4, and mixtures thereof.

44. The gas sensor according to claim 1, wherein the electrolyte is an oxygen ion-conducting electrolyte.

45. The gas sensor according to claim 44, wherein the electrolyte is based on ZrO2, Bi2O3 or CeO2.

46. The gas sensor according to claim 1, wherein the one or more gases are one or more NOx, CO_x, and SO_x.

47. The gas sensor according to claim 1, wherein the one or more gases is NO.

48. The gas sensor according to claim 1, wherein the one or more gases is NO_2.

49. The gas sensor according to claim 1, wherein the one or more gases are NO and NO_2.

50. The gas sensor according to claim 18, wherein a first electrode-pair of the array of electrodes provides a first electrical characteristic providing information with respect to a first of the one or more gases and a second electrode-pair of the array of electrodes provides a second electrical characteristic providing information with respect to a second of the one or more gases.

51. The gas sensor according to claim 50, wherein the first gas is NO and the second gas is NO_2.

52. The gas sensor according to claim 18, wherein a first electrode-pair of the array of electrodes provides a first electrical characteristic providing information with respect to a first of the one or more gases and a second electrode-pair of the array of electrodes provides a second electrical characteristic providing information with respect to the first and a second of the one or more gases.

53. The gas sensor according to claim 50, wherein the first gas is NO_2 and the two gases are NO and NO_2.

54. The gas sensor according to claim 53, wherein the information with respect to the NO and NO_2 is the sum of the concentration of NO and NO_2.

55. The method of sensing one or more gases, comprising:

exposing a sensing electrode to an environment of interest, wherein the sensing electrode is in contact with an electrolyte;

altering the temperature of the sensing electrode; and

measuring an electrical characteristic with respect to the sensing electrode, wherein the measured electrical characteristic provides information with respect to one or more gases in the environment of interest.

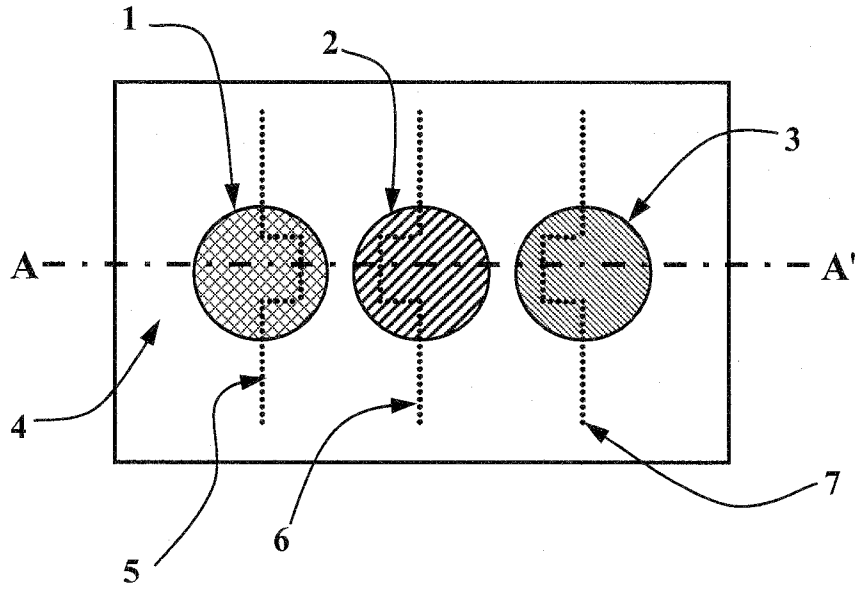

FIG. 1

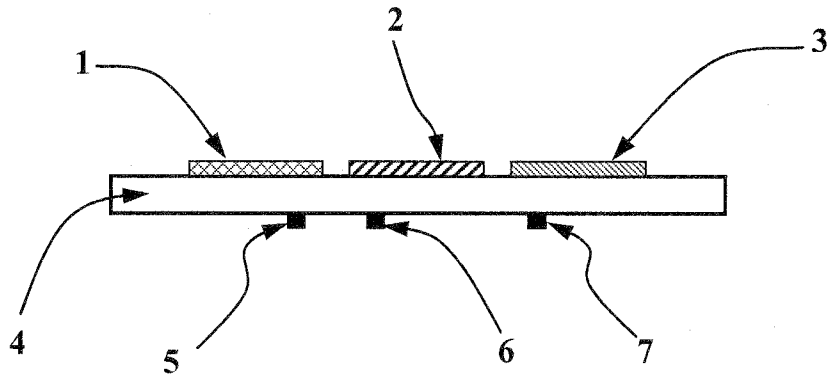

FIG. 2

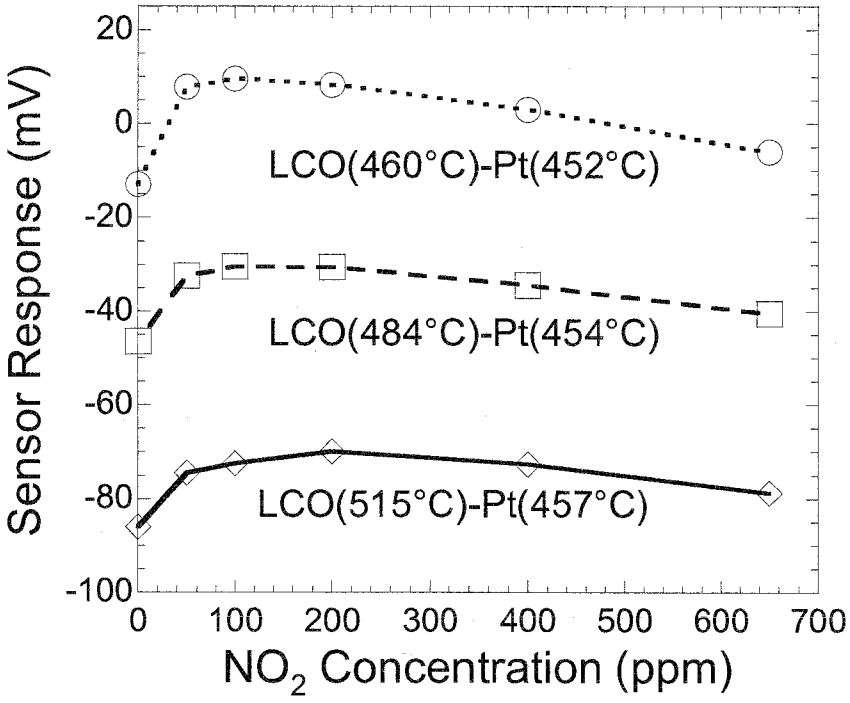
Sensor Response (mV)
20
0
-20
-40
-60
-80
-100
0
100
200
300
400
500
600
700
NO2 Concentration (ppm)
LCO(460°C)-Pt(452°C)
LCO(484°C)-Pt(454°C)
LCO(515°C)-Pt(457°C)

FIG. 3

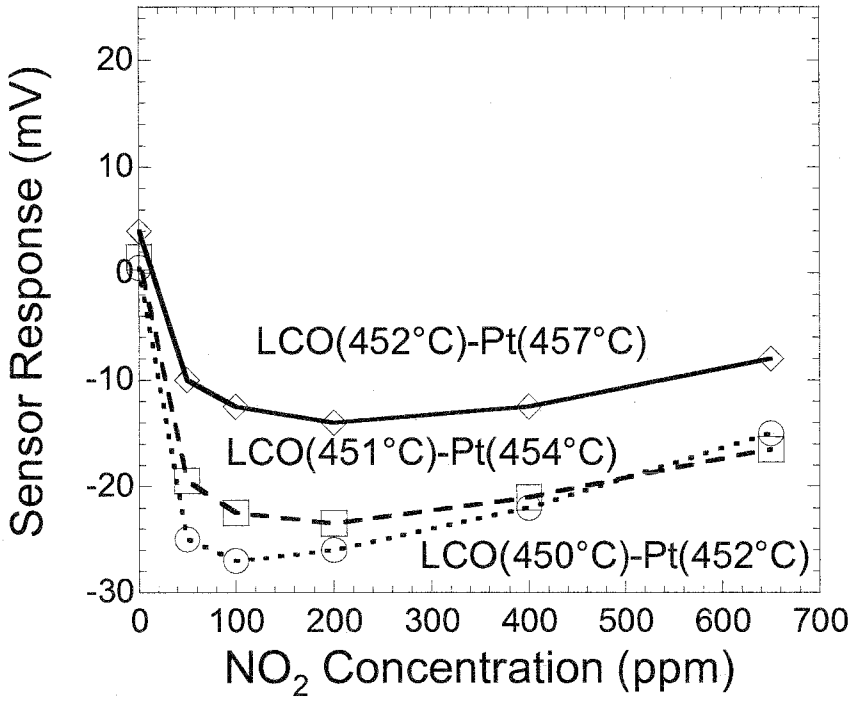
Sensor Response (mV)
20
10
0
-10
-20
-30
0
100
200
300
400
500
600
700
NO2 Concentration (ppm)
LCO(452°C)-Pt(457°C)
LCO(451°C)-Pt(454°C)
LCO(450°C)-Pt(452°C)

FIG. 4

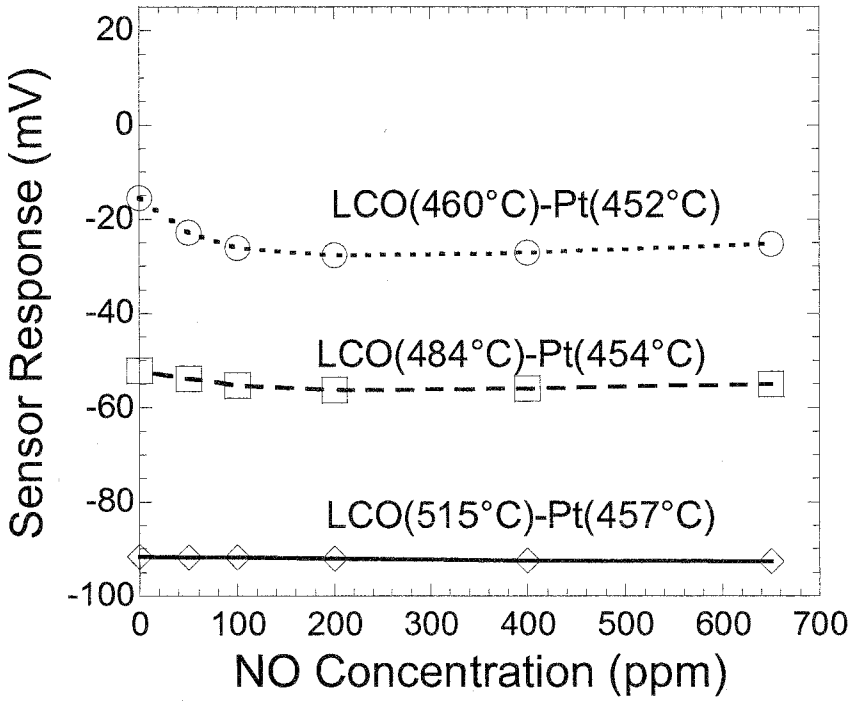
Sensor Response (mV)
20
0
-20
-40
-60
-80
-100
LCO(460°C)-Pt(452°C)
LCO(484°C)-Pt(454°C)
LCO(515°C)-Pt(457°C)
0
100
200
300
400
500
600
700
NO Concentration (ppm)

FIG. 5

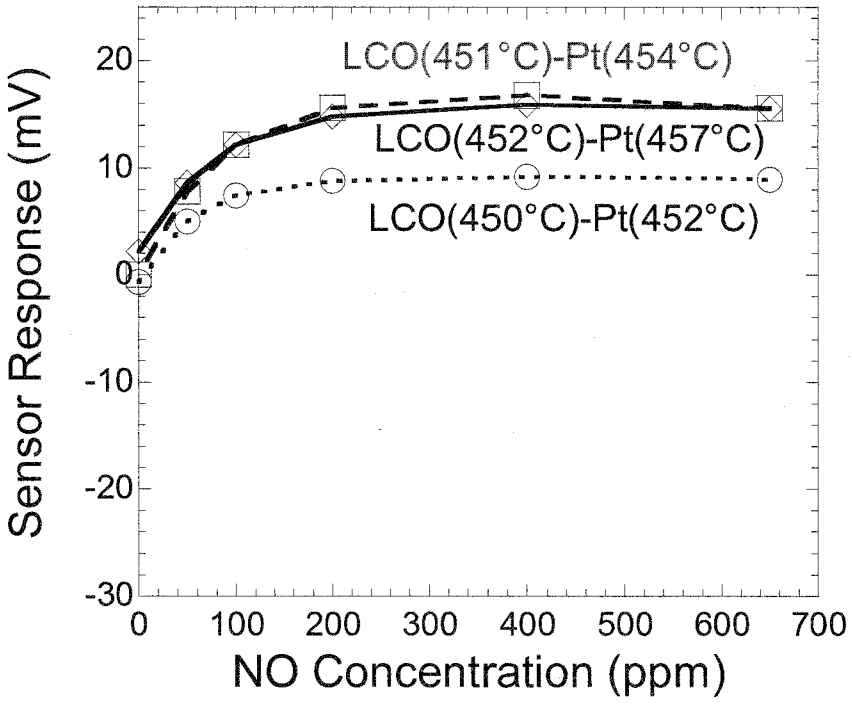
LCO(451°C)-Pt(454°C)
LCO(452°C)-Pt(457°C)
LCO(450°C)-Pt(452°C)
Sensor Response (mV)
NO Concentration (ppm)
20
10
0
-10
-20
-30
0
100
200
300
400
500
600
700

FIG. 6

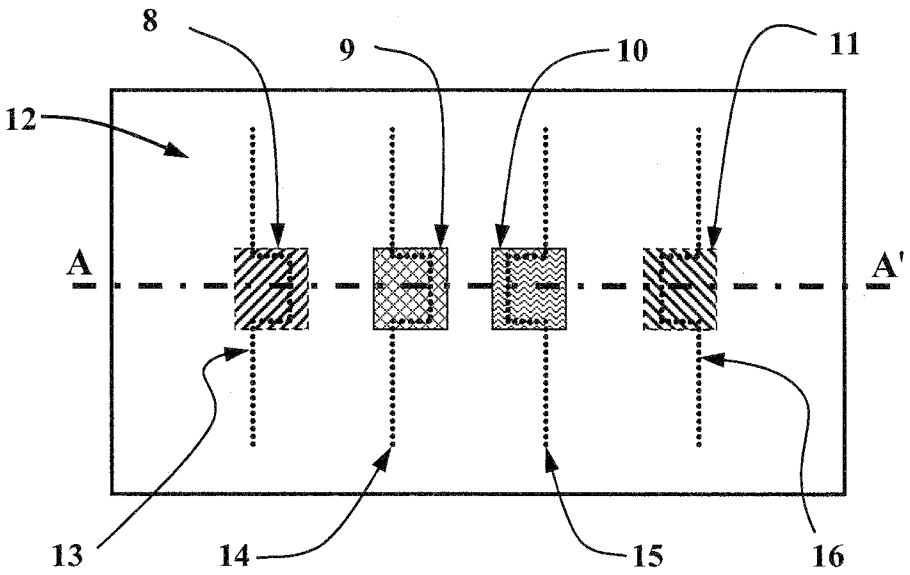

FIG. 7

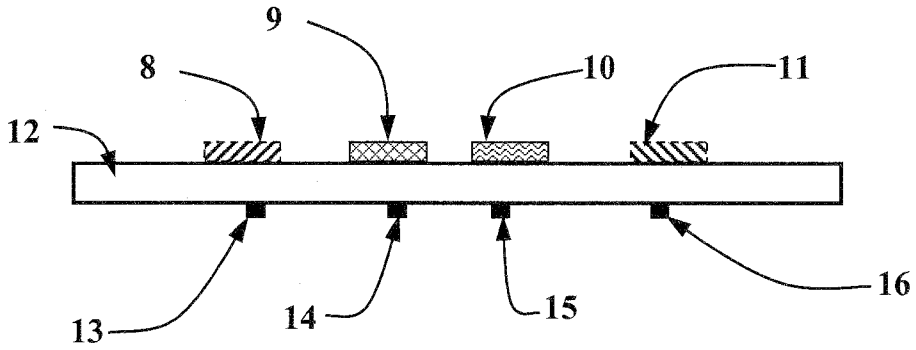

FIG. 8

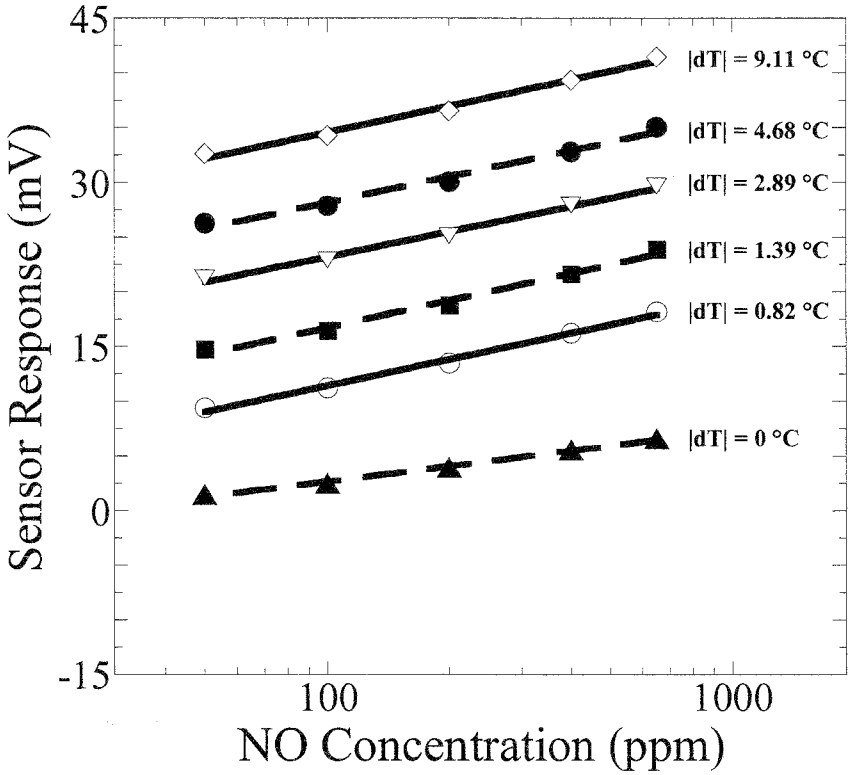
45
30
15
0
-15
Sensor Response (mV)
100
1000
NO Concentration (ppm)
|dT| = 9.11 °C
|dT| = 4.68 °C
|dT| = 2.89 °C
|dT| = 1.39 °C
|dT| = 0.82 °C
|dT| = 0 °C

FIG. 9

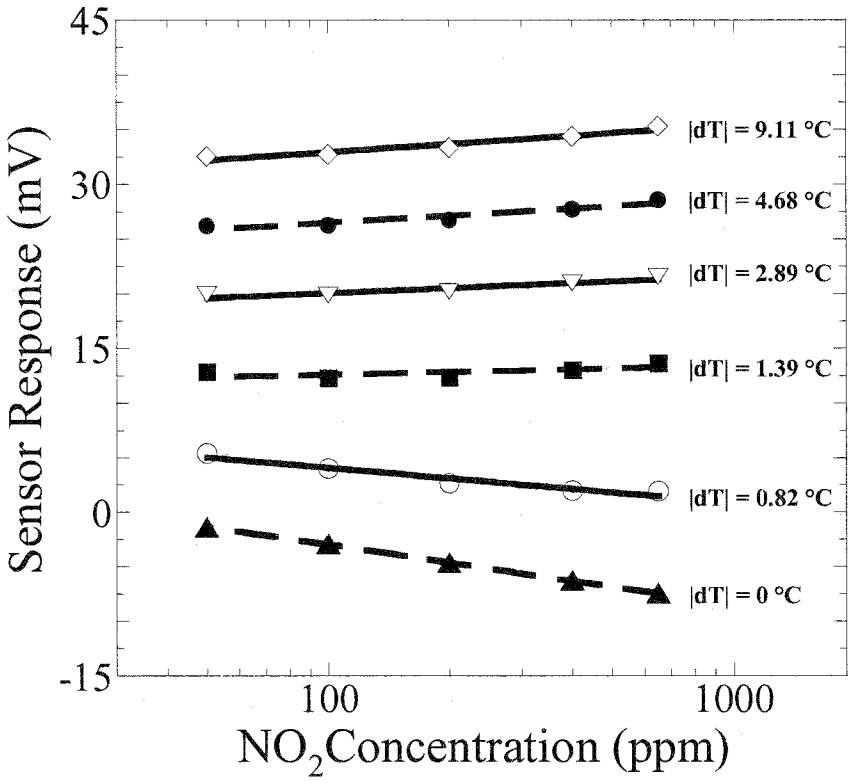
45
30
15
0
-15
Sensor Response (mV)
100
1000
NO2Concentration (ppm)
|dT| = 9.11 °C
|dT| = 4.68 °C
|dT| = 2.89 °C
|dT| = 1.39 °C
|dT| = 0.82 °C
|dT| = 0 °C

FIG. 10

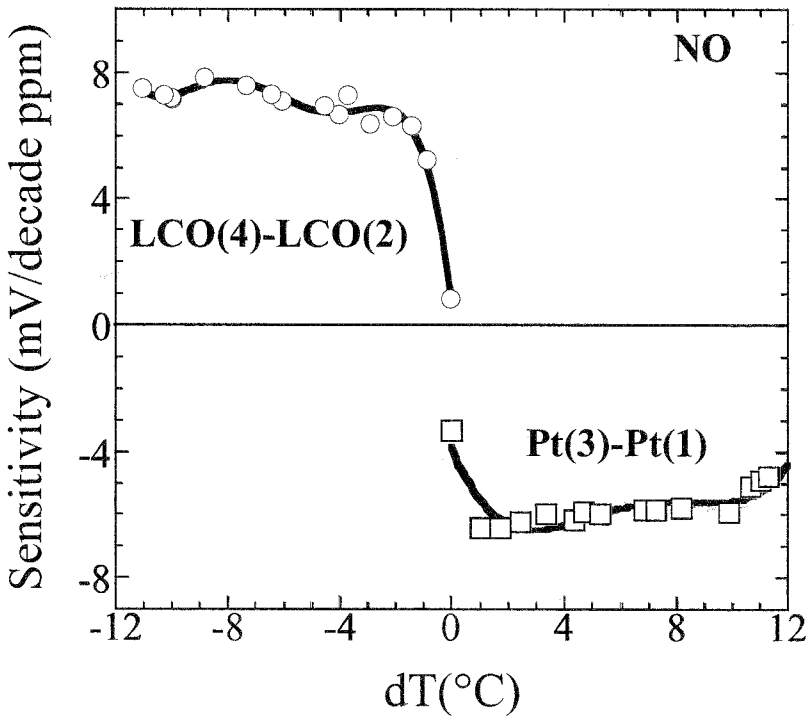
NO
LCO(4)-LCO(2)
Pt(3)-Pt(1)
Sensitivity (mV/decade ppm)
dT(°C)
8
4
0
-4
-8
-12
-8
-4
0
4
8
12

FIG. 11

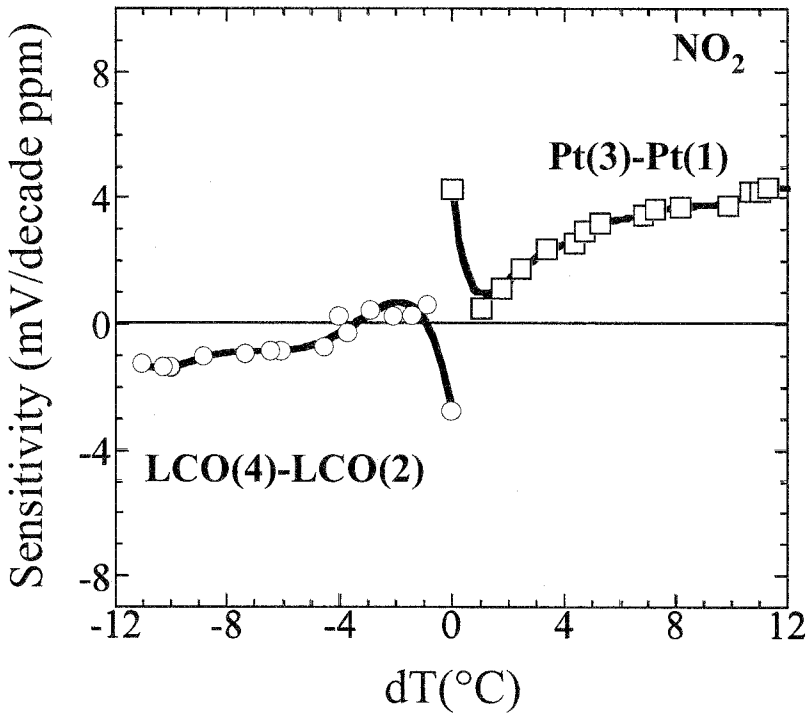
NO2
Pt(3)-Pt(1)
LCO(4)-LCO(2)
Sensitivity (mV/decade ppm)
dT(°C)
8
4
0
-4
-8
-12
-8
-4
0
4
8
12

FIG. 12

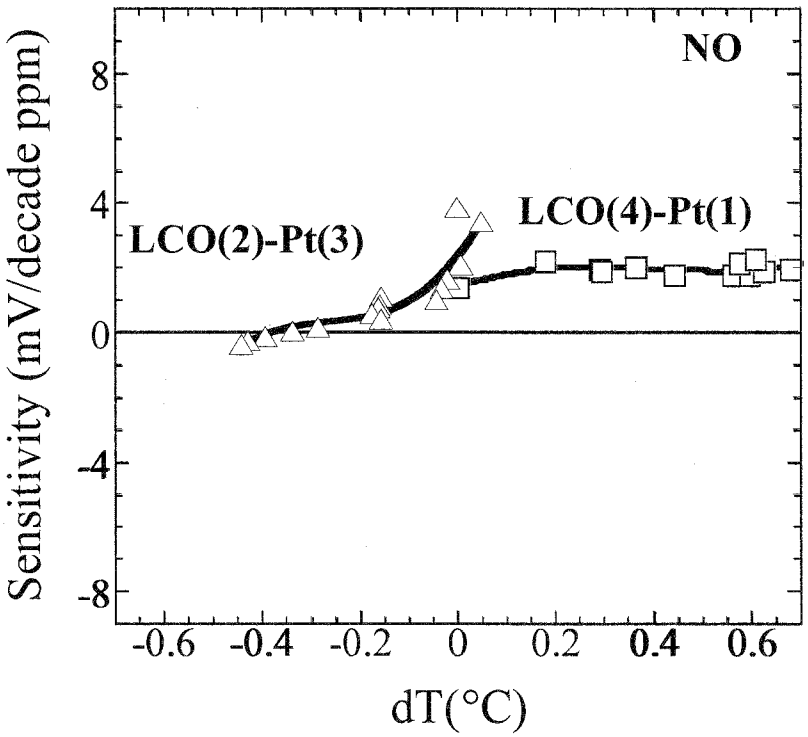
NO
LCO(4)-Pt(1)
LCO(2)-Pt(3)
Sensitivity (mV/decade ppm)
8
4
0
-4
-8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
dT(°C)

FIG. 13

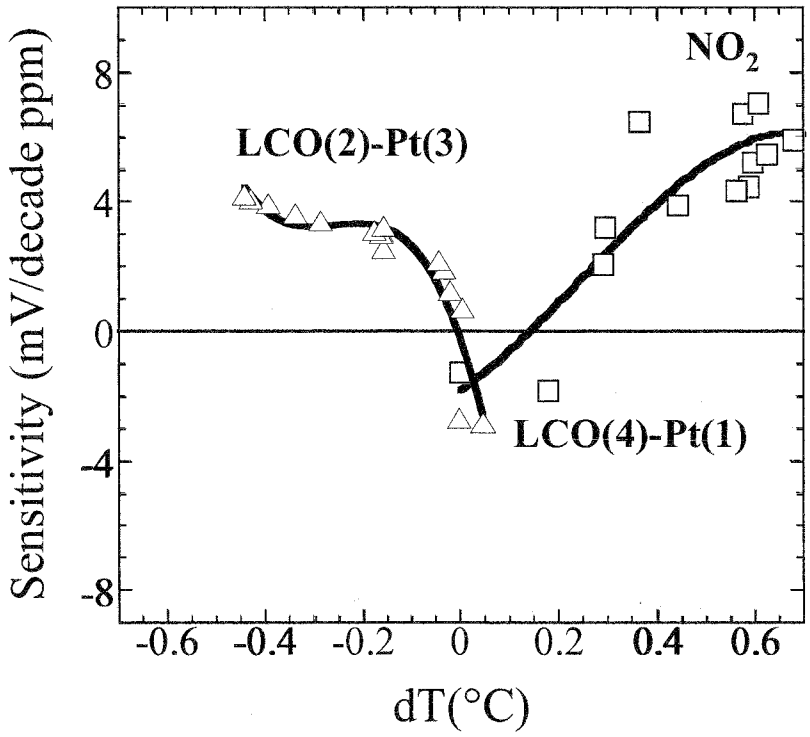
NO2
LCO(2)-Pt(3)
LCO(4)-Pt(1)
Sensitivity (mV/decade ppm)
8
4
0
-4
-8
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
dT(°C)

FIG. 14

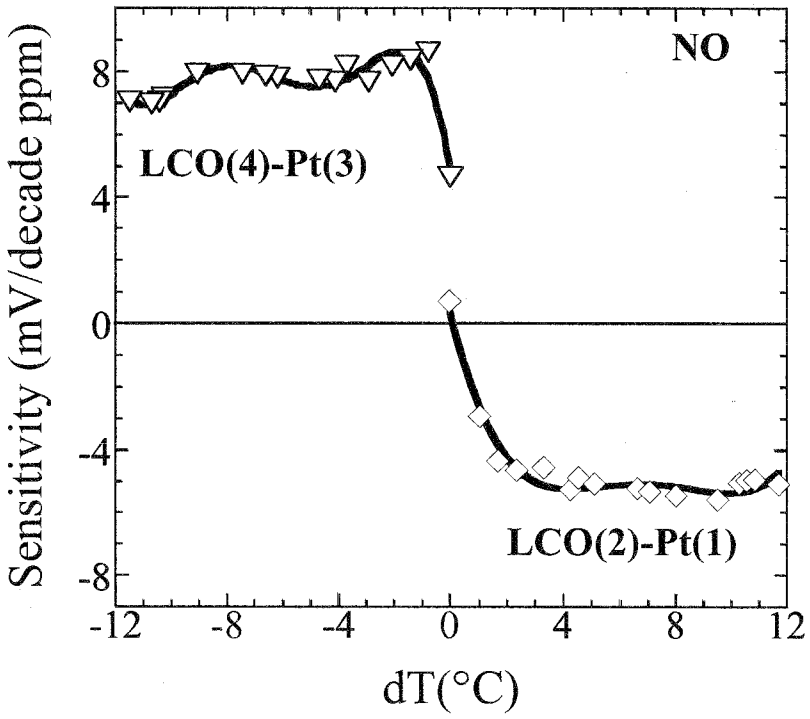
NO
LCO(4)-Pt(3)
LCO(2)-Pt(1)
Sensitivity (mV/decade ppm)
dT(°C)
8
4
0
-4
-8
-12
-8
-4
0
4
8
12

FIG. 15

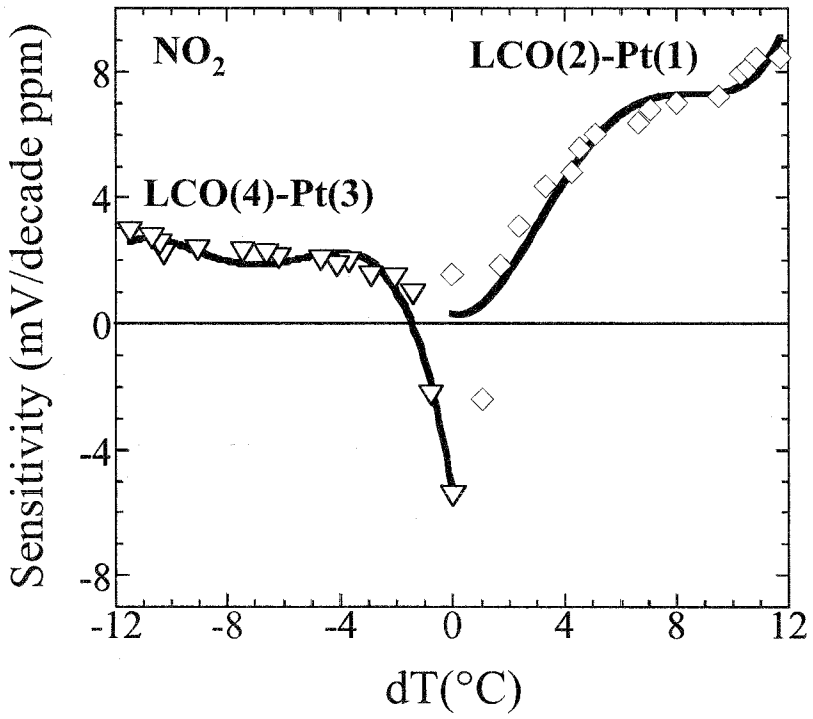
NO2
LCO(2)-Pt(1)
LCO(4)-Pt(3)
Sensitivity (mV/decade ppm)
dT(°C)
8
4
0
-4
-8
-12
-8
-4
0
4
8
12

FIG. 16

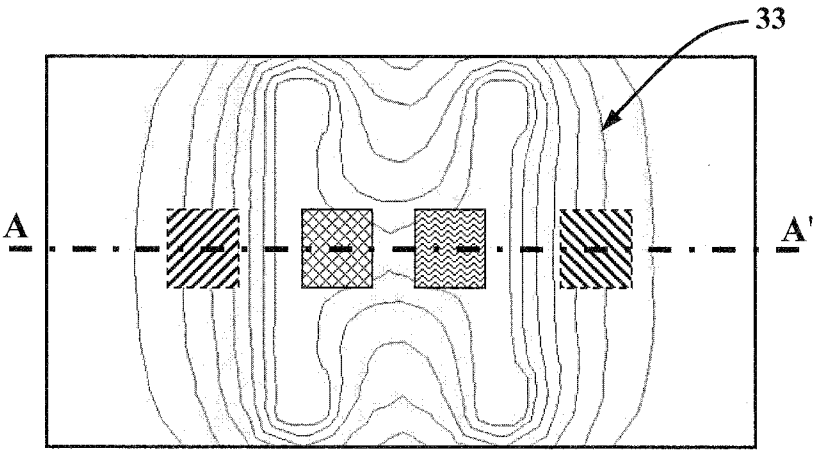

FIG. 17A

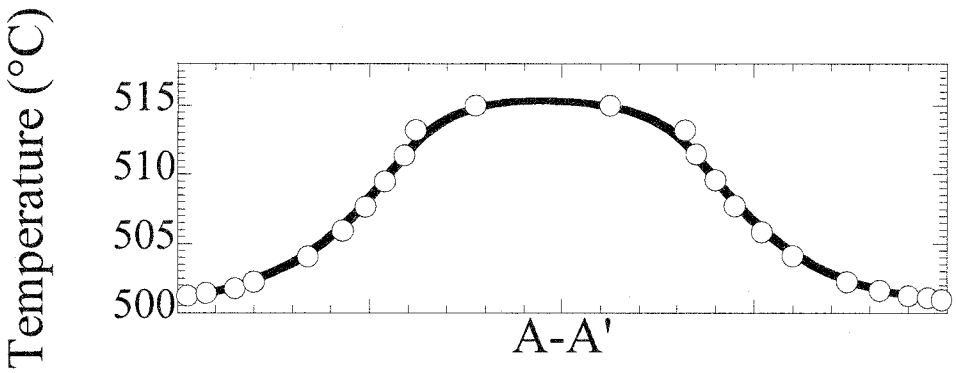

FIG. 17B

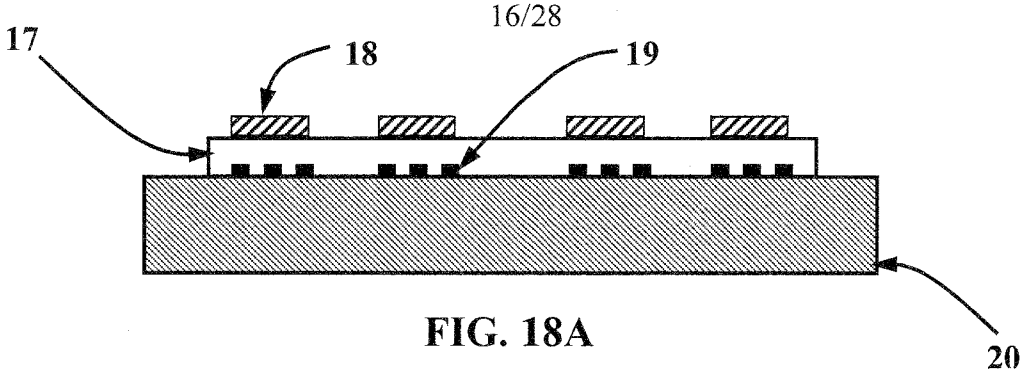

FIG. 18A

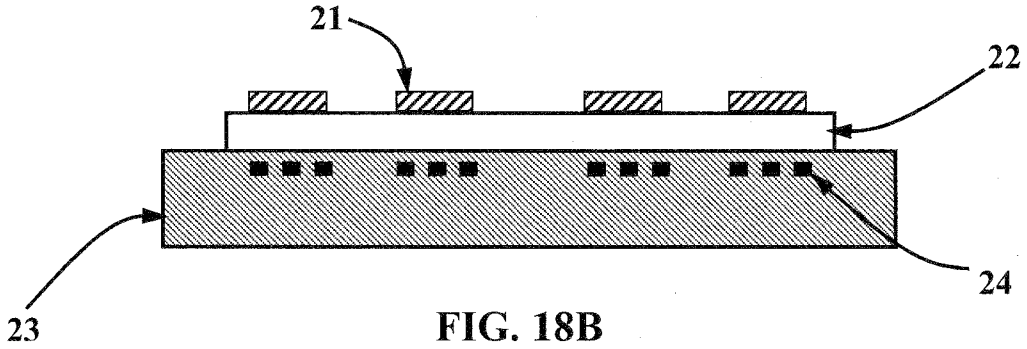

FIG. 18B

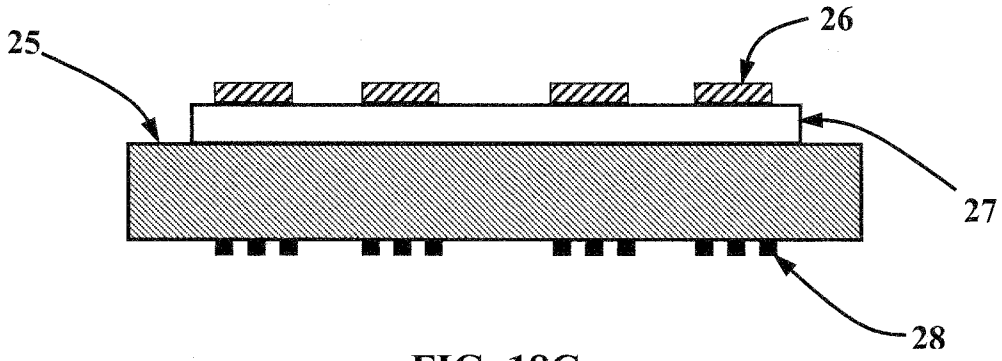

FIG. 18C

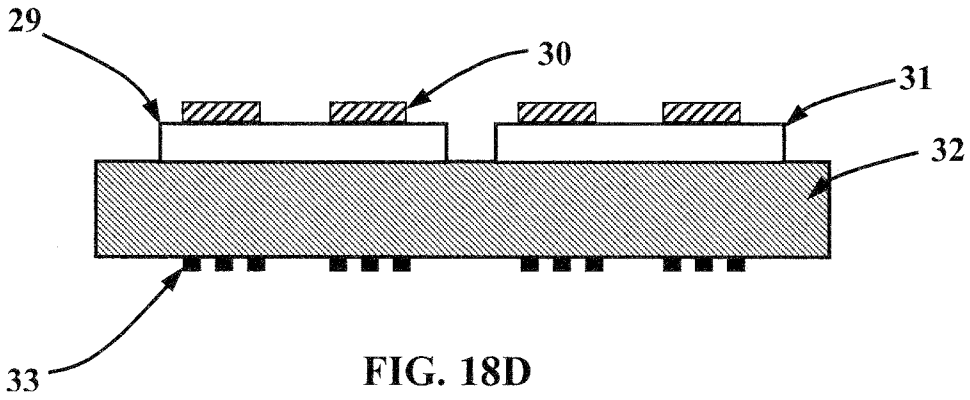

FIG. 18D

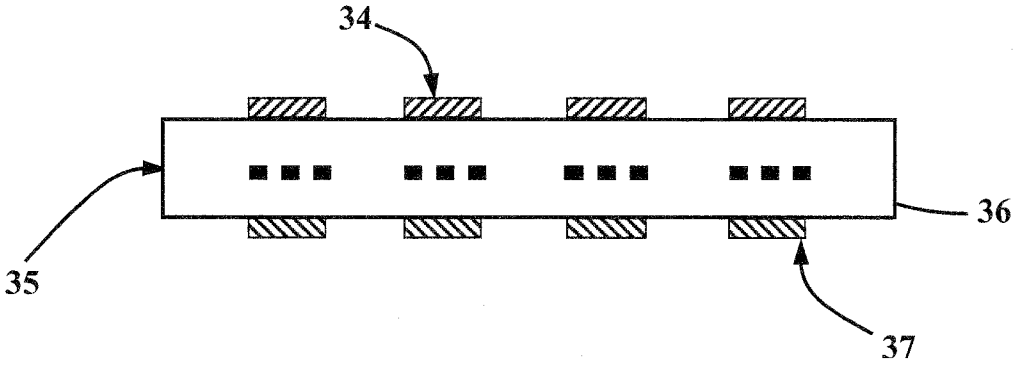

FIG. 19

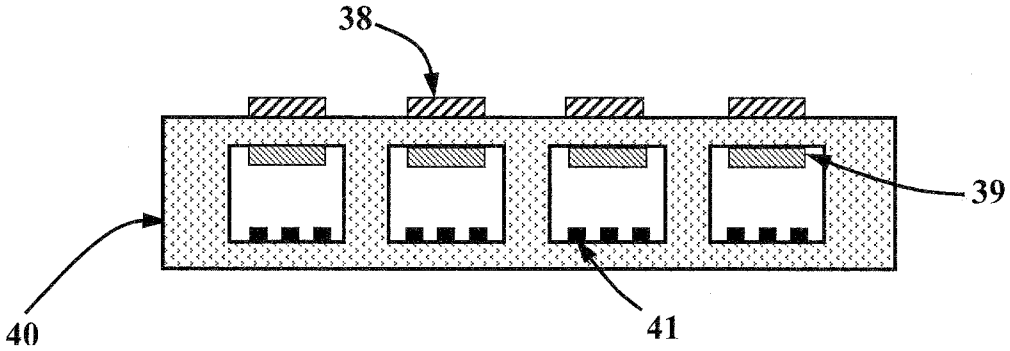

FIG. 20

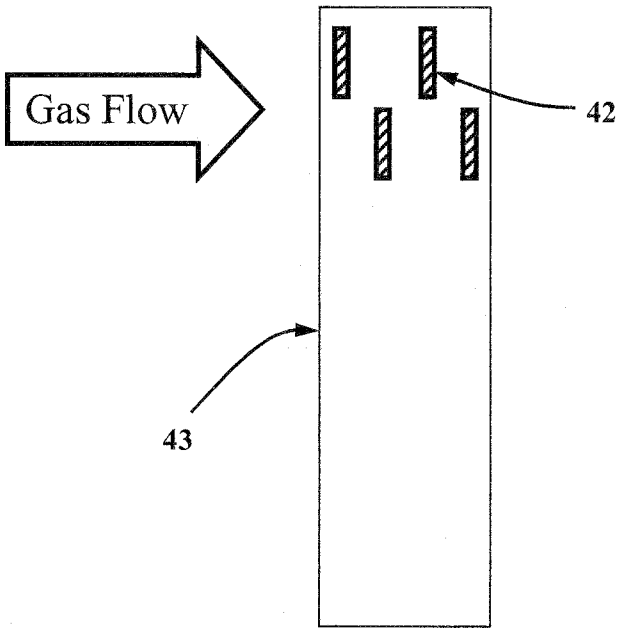

FIG. 21A

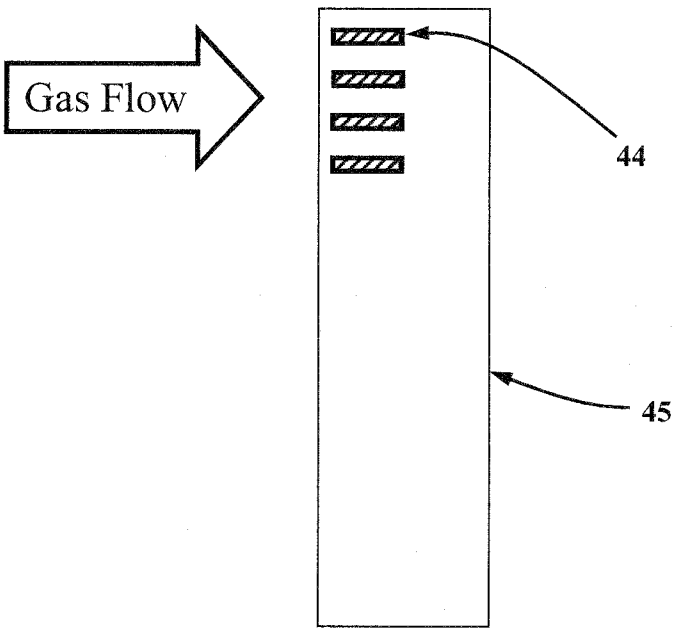

FIG. 21B

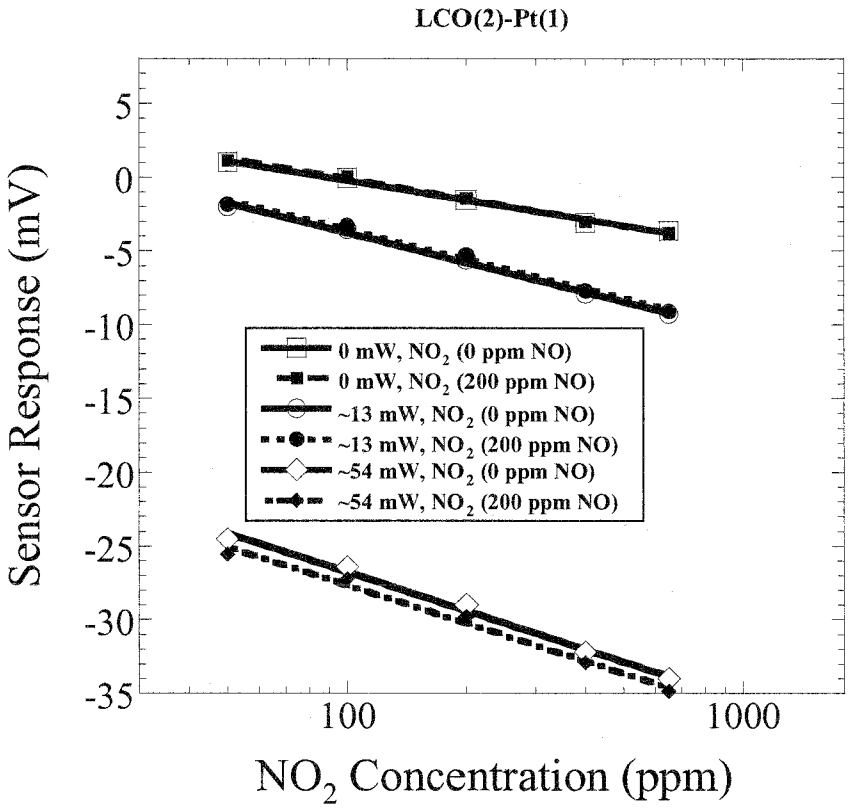
LCO(2)-Pt(1)
Sensor Response (mV)
5
0
-5
-10
-15
-20
-25
-30
-35
100
1000
NO2 Concentration (ppm)
0 mW, NO2 (0 ppm NO)
0 mW, NO2 (200 ppm NO)
~13 mW, NO2 (0 ppm NO)
~13 mW, NO2 (200 ppm NO)
~54 mW, NO2 (0 ppm NO)
~54 mW, NO2 (200 ppm NO)

FIG. 22

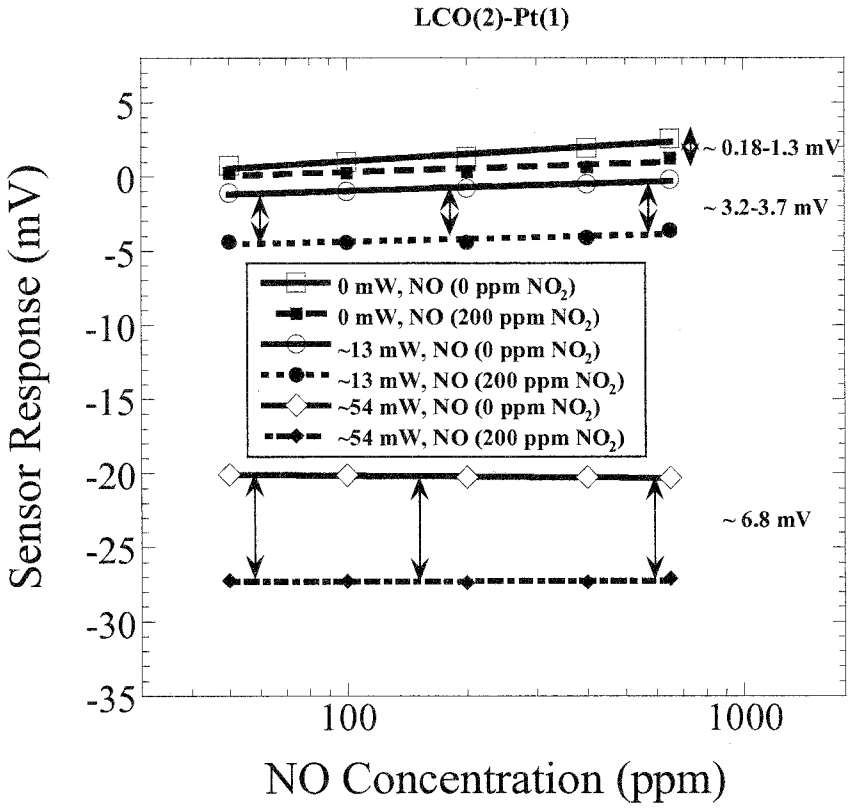
LCO(2)-Pt(1)
Sensor Response (mV)
5
0
-5
-10
-15
-20
-25
-30
-35
100
1000
NO Concentration (ppm)
~ 0.18-1.3 mV
~ 3.2-3.7 mV
~ 6.8 mV
0 mW, NO (0 ppm NO2)
0 mW, NO (200 ppm NO2)
~13 mW, NO (0 ppm NO2)
~13 mW, NO (200 ppm NO2)
~54 mW, NO (0 ppm NO2)
~54 mW, NO (200 ppm NO2)

FIG. 23

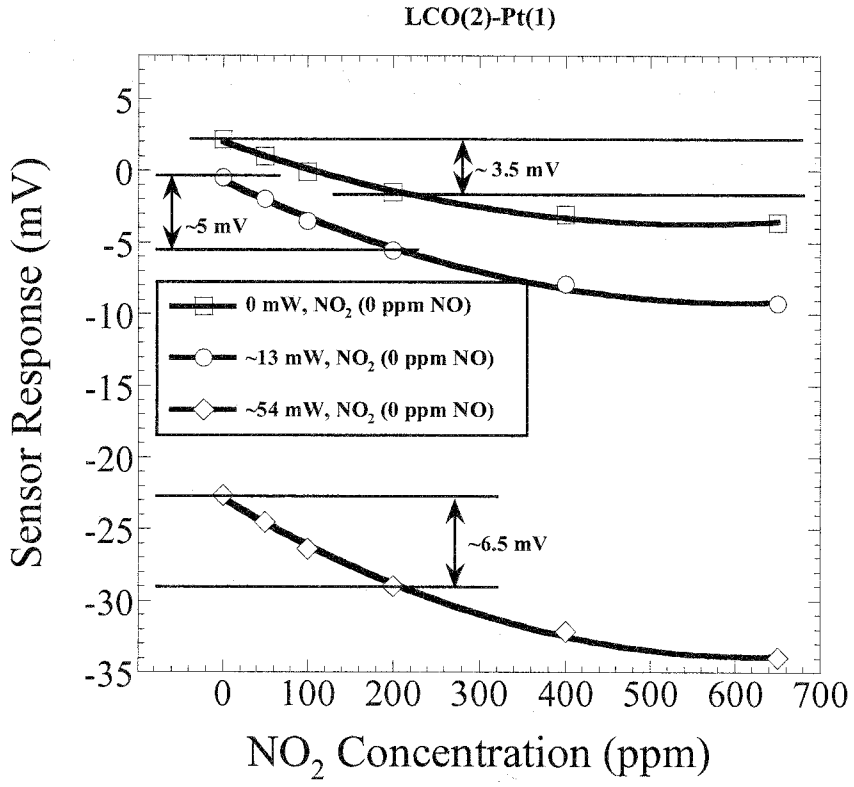
LCO(2)-Pt(1)
Sensor Response (mV)
5
0
-5
-10
-15
-20
-25
-30
-35
~3.5 mV
~5 mV
0 mW, NO2 (0 ppm NO)
~13 mW, NO2 (0 ppm NO)
~54 mW, NO2 (0 ppm NO)
~6.5 mV
0
100
200
300
400
500
600
700
NO2 Concentration (ppm)

FIG. 24

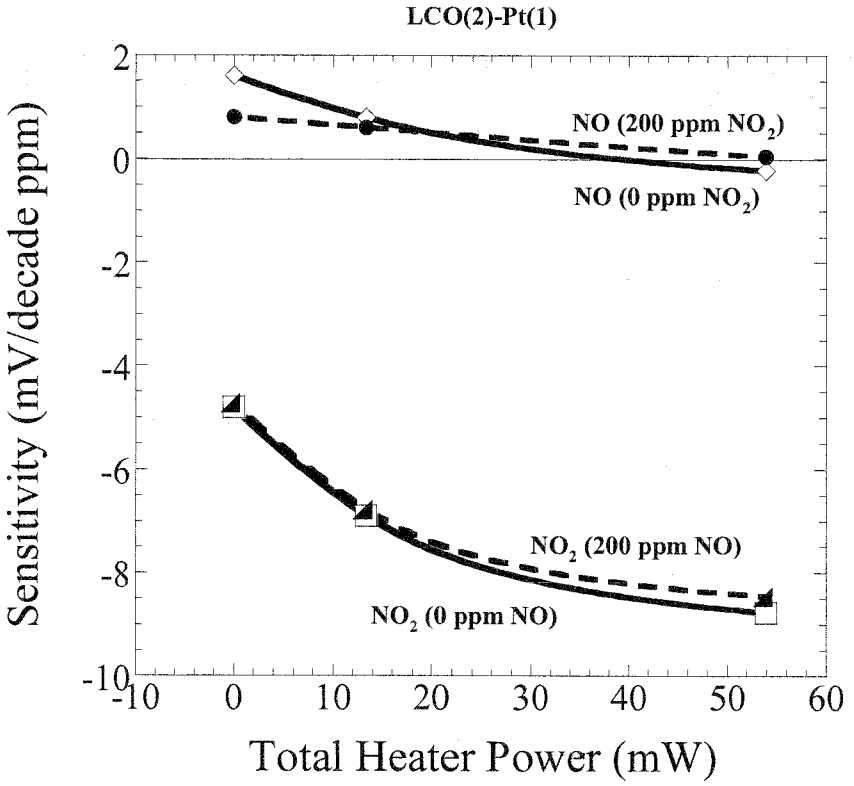
LCO(2)-Pt(1)
Sensitivity (mV/decade ppm)
Total Heater Power (mW)
NO (200 ppm NO2)
NO (0 ppm NO2)
NO2 (200 ppm NO)
NO2 (0 ppm NO)
2
0
-2
-4
-6
-8
-10
-10
0
10
20
30
40
50
60

FIG. 25

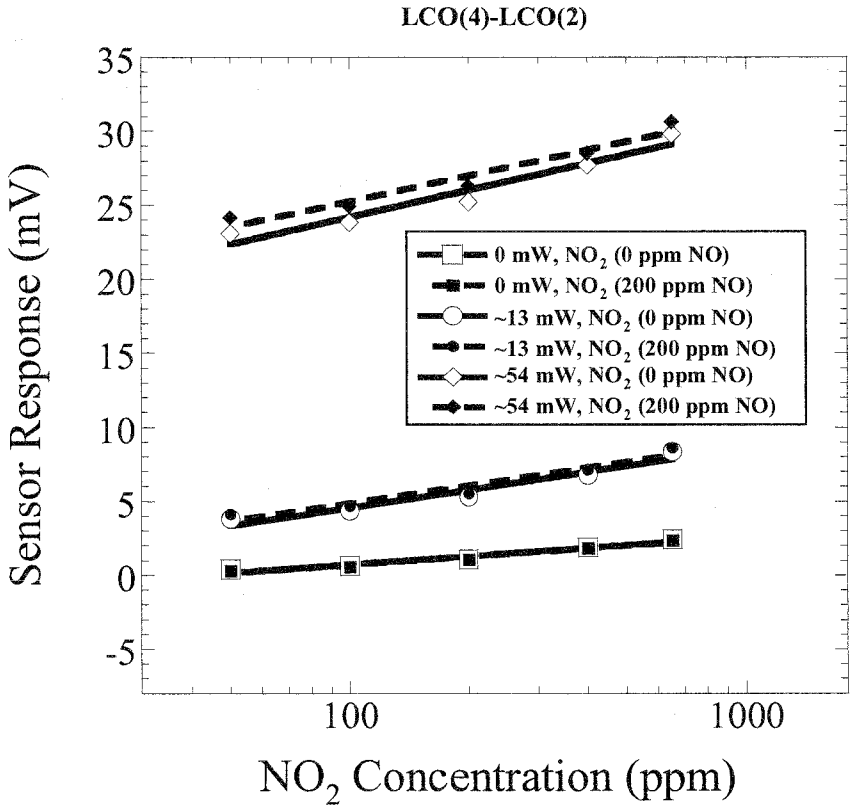
LCO(4)-LCO(2)
Sensor Response (mV)
35
30
25
20
15
10
5
0
-5
100
1000
NO2 Concentration (ppm)
0 mW, NO2 (0 ppm NO)
0 mW, NO2 (200 ppm NO)
~13 mW, NO2 (0 ppm NO)
~13 mW, NO2 (200 ppm NO)
~54 mW, NO2 (0 ppm NO)
~54 mW, NO2 (200 ppm NO)

FIG. 26

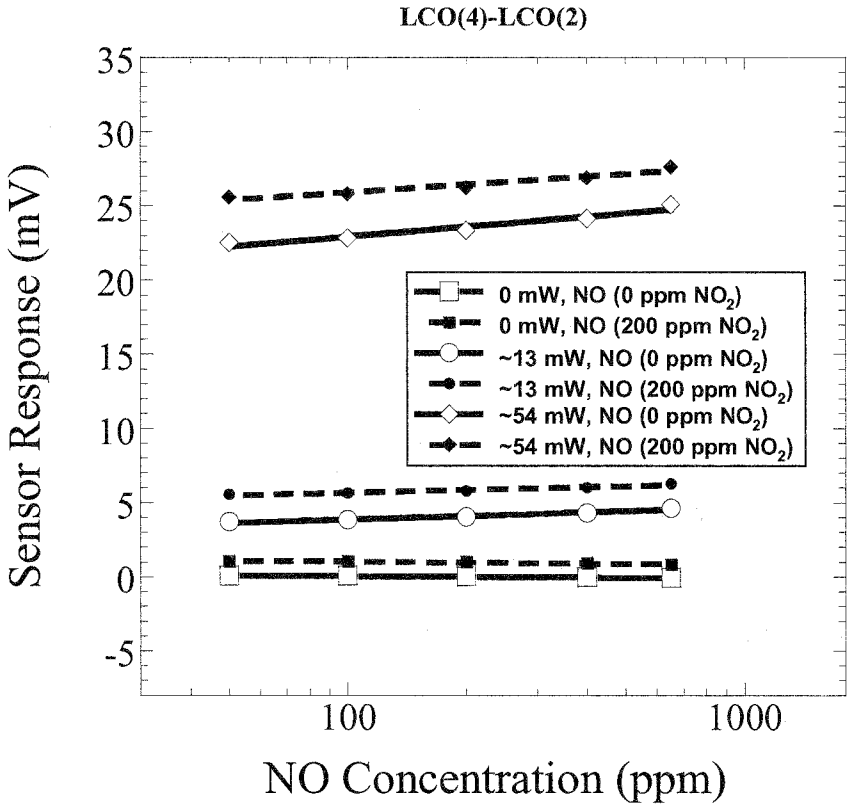
LCO(4)-LCO(2)
Sensor Response (mV)
35
30
25
20
15
10
5
0
-5
100
1000
NO Concentration (ppm)
0 mW, NO (0 ppm NO2)
0 mW, NO (200 ppm NO2)
~13 mW, NO (0 ppm NO2)
~13 mW, NO (200 ppm NO2)
~54 mW, NO (0 ppm NO2)
~54 mW, NO (200 ppm NO2)

FIG. 27

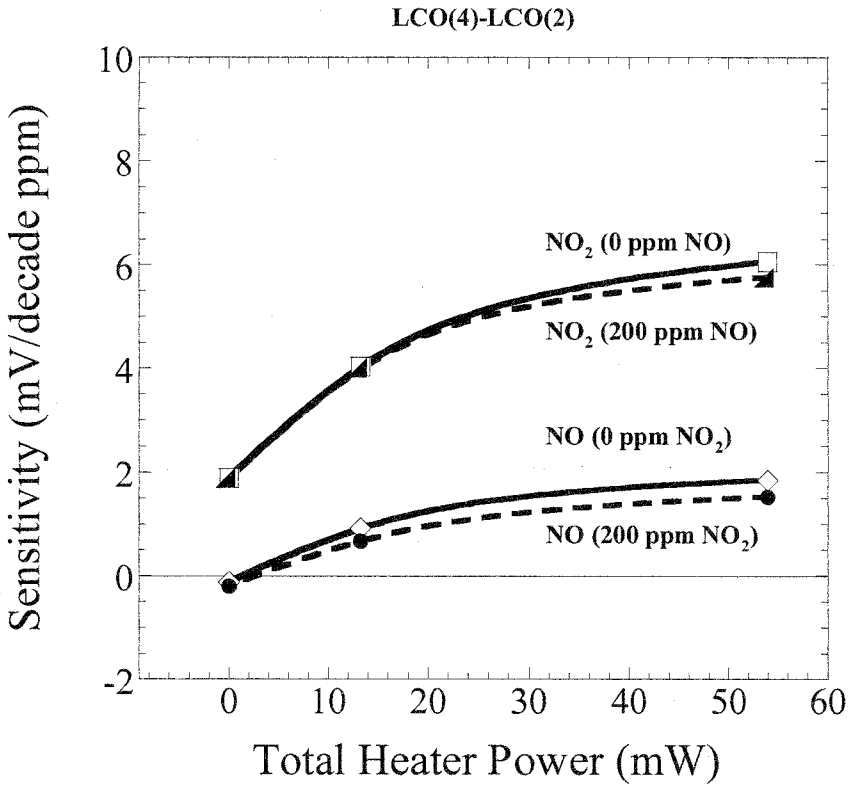
LCO(4)-LCO(2)
Sensitivity (mV/decade ppm)
Total Heater Power (mW)
NO2 (0 ppm NO)
NO2 (200 ppm NO)
NO (0 ppm NO2)
NO (200 ppm NO2)
10
8
6
4
2
0
-2
0
10
20
30
40
50
60

FIG. 28

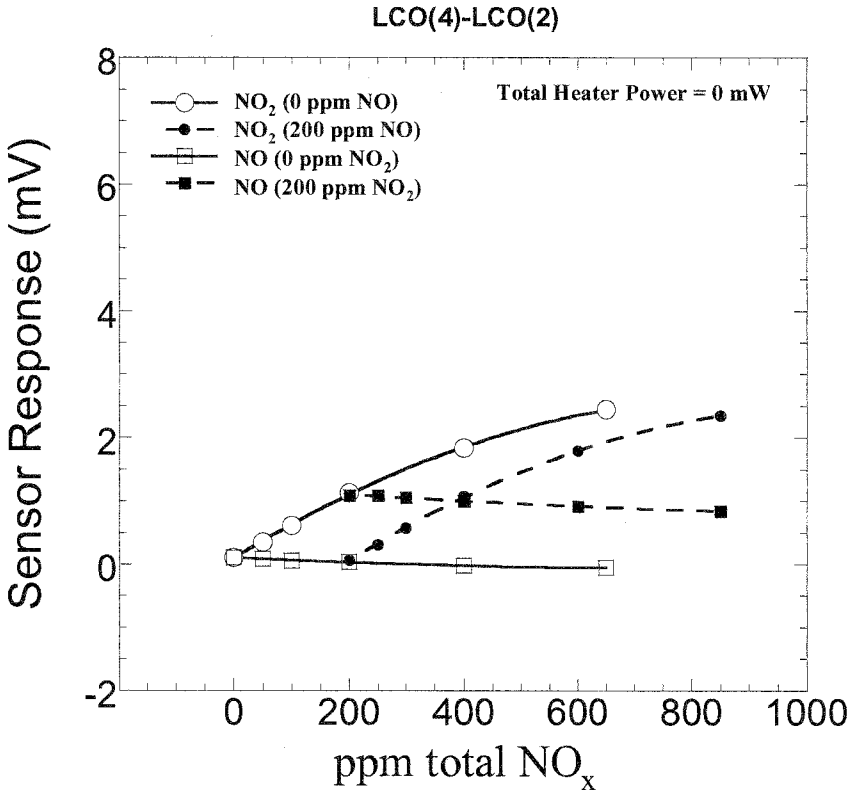
LCO(4)-LCO(2)
Total Heater Power = 0 mW
NO2 (0 ppm NO)
NO2 (200 ppm NO)
NO (0 ppm NO2)
NO (200 ppm NO2)
Sensor Response (mV)
8
6
4
2
0
-2
0
200
400
600
800
1000
ppm total NOx

FIG. 29

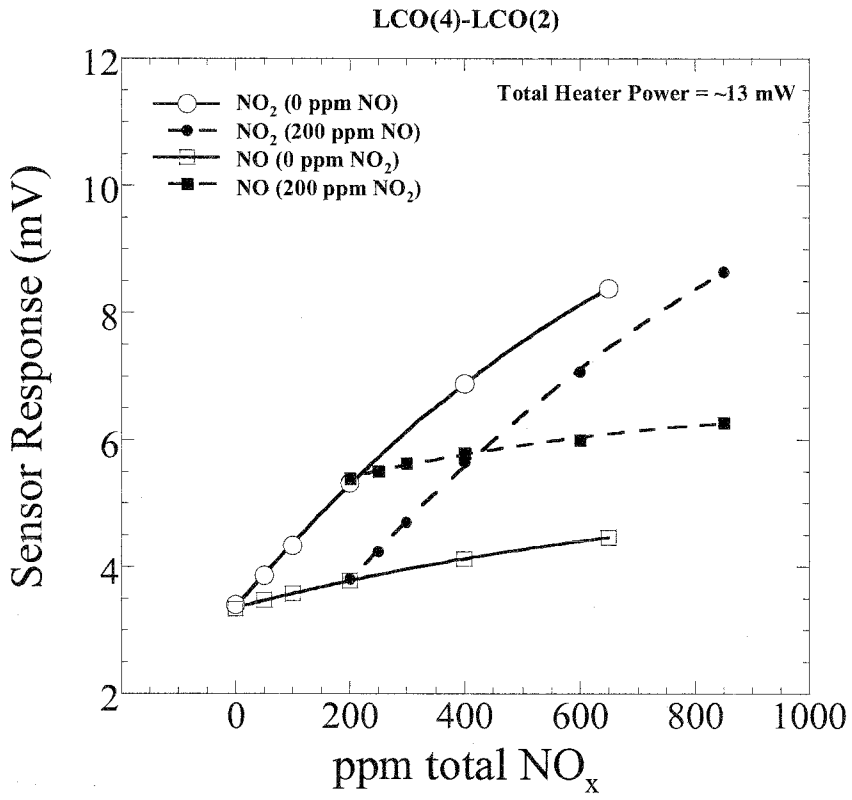
LCO(4)-LCO(2)
Total Heater Power = ~13 mW
NO2 (0 ppm NO)
NO2 (200 ppm NO)
NO (0 ppm NO2)
NO (200 ppm NO2)
Sensor Response (mV)
ppm total NOx
12
10
8
6
4
2
0
200
400
600
800
1000

FIG. 30

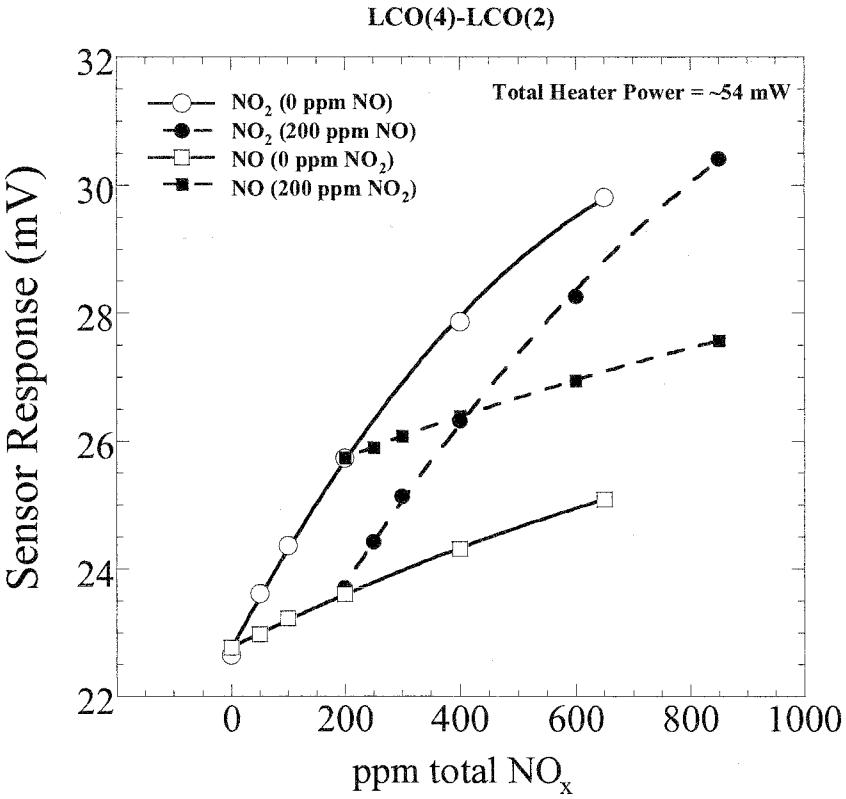
LCO(4)-LCO(2)
Total Heater Power = ~54 mW
NO2 (0 ppm NO)
NO2 (200 ppm NO)
NO (0 ppm NO2)
NO (200 ppm NO2)
Sensor Response (mV)
32
30
28
26
24
22
0
200
400
600
800
1000
ppm total NOx

FIG. 31