Catalytic hydrogen sensing using microheated platinum nanoparticle-loaded graphene aerogel

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Abstract

Low power catalytic hydrogen sensors are fabricated by functionalizing low power polysilicon microheaters with platinum nanoparticle catalyst loaded in a high surface area graphene aerogel support. Fabrication and characterization of the polysilicon microheaters are described. The platinum nanoparticle-loaded graphene aerogel is characterized by transmission electron microscopy, scanning electron microscopy, and energy dispersive x-ray spectroscopy. The catalytic hydrogen sensors consume as little as 2.2 mW of power, have sensitivity of 1.6%/10,000 ppm hydrogen, a t_{90} response and recovery time of 0.97 s and 0.72 s, respectively, a lower detection limit of approximately 65 ppm, and negligible cross sensitivity to methane, n-pentane, and diethylether.

Keywords: catalytic gas sensing, microheaters, graphene aerogel, platinum nanoparticles, low power hydrogen sensing

1. Introduction

Hydrogen is an important industrial gas used in a variety of applications, and has become especially popular as an alternative fuel for transportation. As hydrogen is odorless, colorless, and flammable, it is critical to install hydrogen gas monitoring systems that can detect potentially explosive situations [1]. Several different sensing schemes exploiting various chemical properties of hydrogen have come under consideration and development [2], including catalytic combustion sensors[3,4], thermal conductivity sensors[5,6], electrochemical sensors [7,8], semiconducting metal-oxide sensors [9], and metallic resistors [10,11].

Catalytic combustion sensors are widely used in industry. However, the catalyst must be heated to high temperature in order to promote hydrogen combustion, resulting in relatively high power consumption. These sensors consist of a Joule-heated platinum wire coated with a catalyst-containing support material, typically a ceramic. The catalyst promotes combustion, generating heat, causing the temperature of the Pt wire to increase. This increase in temperature causes an increase in the resistance of the Pt wire. The change in resistance is typically measured using a Wheatstone bridge configuration with a reference element that is identical minus the catalyst to offset atmospheric changes in temperature or humidity. While these sensors are widely deployed, their relatively high level of power consumption has impeded their implementation as long-term, battery-powered monitors. Advances in microelectromechanical systems (MEMS) technology have allowed for decreased power consumption through device miniaturization[3,12]. For a typical MEMS catalytic combustion sensor, a microfabricated Pt or polysilicon heating element, or microheater, is embedded in a thin silicon nitride membrane upon which a catalyst layer is deposited. Due to scaling laws, the drastic reduction in size of the microheater provides a corresponding reduction in thermal response time. The short thermal response time allows for rapid heating and cooling of the device, thereby enabling low duty cycle operation and further reduction in power consumption.

Many of the reported microheater-based hydrogen gas sensors use a catalyst layer of Pt or Pd nanoparticles dispersed in a porous alumina or silica support.[4,13,14] Recent work by Brauns, et al.[15] employs Pt nanoparticles stabilized with surfactant molecules eliminating the need for a porous ceramic support, thereby reducing the thermal mass (hence lowering the power consumption) and transferring heat more efficiently (leading to higher sensitivity and faster response time). However, due to the thermal instability of the surfactant, these sensors are not amenable to high temperature application or operation.

Here we report the fabrication and characterization of a catalytic hydrogen sensor using platinum (Pt) nanoparticle catalyst embedded in graphene aerogel catalyst support. The Pt nanoparticle-loaded graphene aerogel is deposited on a low power polysilicon-based microheater device, which is used to both heat the catalyst and detect the heat output from the catalytic combustion of hydrogen. The synthesis and characterization of the graphene aerogel and platinum functionalization are described. The measurement of the catalytic hydrogen sensor is described and optimized for sensitivity, selectivity, and stability.

2. Experimental

2.1 Microheater fabrication & characterization

Microheaters are fabricated using 4-mask surface micromachining process to create a polysilicon microheater embedded in a thin silicon nitride membrane, as shown schematically in Figure 1. First, a 100 nm thick film of low-stress silicon nitride (LSN) is deposited on a silicon wafer by low-pressure chemical vapor deposition (LPCVD). This is followed by deposition of 150 nm in-situ doped polysilicon and 2 μm boron doped silicon dioxide. The wafers are then heated to 1050 $^{\circ}\text{C}$ for film stress release, dopant diffusion, and dopant activation in the polysilicon layer. The oxide layer is then removed in buffered hydrogen fluoride (BHF) etch

bath. The microheater is then patterned into the polysilicon layer using photolithography and reactive ion etching. This is followed by another 100-nm-thick LSN layer deposition to encapsulate the polysilicon microheater. Contact to the microheaters is made by patterning and removing the upper LSN layer by reactive ion etching and subsequent deposition of 10 nm of titanium and 90 nm of platinum. The wafers are then annealed in nitrogen environment at 350 °C for 1 hour to release Pt film stress. Finally, the wafers are patterned and KOH etched from the backside to remove the silicon under the microheaters leaving only the thin silicon nitride membrane.

The wafer is then diced into 3.5 x 3.5 mm² chips, which typically contain four individual microheaters per chip. The microheaters used in this work are 10 μm wide, 100 μm long, and 100 nm thick. Once individualized, the microheater chips are wire-bonded into a 14-pin cer-dip package for electrical characterization.

2.2 Synthesis & characterization of Pt nanoparticle-loaded graphene aerogel

Graphene aerogel is prepared using a precursor of graphene oxide prepared with Hummer's method. Organic sol-gel chemistry is used to cross-link the sheets and after supercritical drying, carbonization is achieved through pyrolysis at 1050 °C under nitrogen [16,17]. To decorate with Pt nanoparticles, the graphene aerogels are submerged in an aqueous solution of 0.5M chloroplatinic acid. The aerogels are then freeze dried to ensure even distribution of the platinum salt. Finally, the platinum salt is reduced to platinum metal by heating under hydrogen gas at 450 °C [18].

The loading and size distribution of the Pt nanoparticles deposited on the graphene aerogel is characterized using transmission electron microscopy (TEM, JEOL 2010) and scanning electron microscopy (SEM, FEI Sirion XL30). Energy dispersive x-ray spectroscopy (EDAX) is used for elemental analysis.

2.3 Fabrication of gas sensor

The platinum nanoparticle-loaded graphene aerogel material is sonicated into suspension and deposited from a solution of isopropyl alcohol. A 0.25 μL drop of 0.5 mg/mL solution is placed on the microheater chip while the microheater is powered to 8 mW (~220 °C). Heating the microheater promotes solvent evaporation and leads to material deposition at the center of the microheater. The microheater heated at 8 mW for 3 hours to ensure all the solvent is evaporated.

2.4 Gas delivery

The microheater cer-dip package is placed within a gas flow chamber with a volume of 1 cm³. The sensor is exposed to hydrogen using a computer-controlled gas delivery system. A cylinder of 3% hydrogen gas balanced in nitrogen is used (Praxair). For selectivity tests, sensors are exposed to various concentrations of diethylether (Praxair, 5000 ppm in N₂), n-pentane (Praxair, 5000 ppm in N₂), and methane (Praxair, 5% in N₂) using the same gas delivery system. Sensor testing is performed at a constant flow rate of 300 sccm. Stream balance and purge is made up of house air that has passed through pressure swing adsorption dryers to

remove humidity and an activated carbon scrubber to remove other contaminants. Mass flow controllers (Bronkhorst) controlled by LabView are used to dilute the gas mixture cylinder with clean air and deliver these gases to the sensor chamber. Flow stream temperatures are recorded and are within a few degrees of room temperature. In all but one test, the gas mixture from the analyte gas cylinder is mixed with clean air to attain the desired analyte concentration. In these tests, the oxygen concentration in the gas stream is at least 12 times the stoichiometric concentration to oxidize the hydrogen to form water. The exception is for the test performed in pure nitrogen to show the lack of catalytic response in the absence of oxygen (Supplementary Figure S2).

2.5 Microheater sensor measurement

The measurement of the microheater sensor is performed using a Keithley 2602 source-meter. The source-meter is controlled using Zephyr [19], an open-source Java-based instrument and control and measurement software suite. Zephyr is also used to acquire data from the source-meter, the gas delivery system, such as flow rates and concentrations, and any reference sensors, such as temperature sensors. The microheater sensors are measured either by continuously applying a bias voltage or by pulsing the heater to a particular voltage for a specified amount of time. The current through the microheater is recorded and its resistance, R , is calculated. Sequences comprised of multiple voltage pulses are used to quickly change the sensor temperature and these pulse sequences are continually repeated after a specified period. The sensor response is determined by the relative change in resistance, $\Delta R/R_0$, which is defined as $\frac{R - R_0}{R_0}$, where R is the average resistance during exposure to a given hydrogen concentration and R_0 is the average resistance during zero hydrogen exposure.

3. Results & Discussion

Polysilicon is chosen for the microheater element for its high and tunable resistivity, compatibility with MEMS processing, and its resistance to electromigration [20-22]. These properties allow very small microheaters to be fabricated using a scalable process with high power density yet minimal total power. Polysilicon also allows for multiple devices to be fabricated onto a single millimeter-sized chip, which is exceedingly difficult to do with metallic microheaters. While a suspended beam geometry would be the most thermally efficient microheater, since power lost to the substrate would be lower, for ease of sensor fabrication we choose to employ a thin, suspended silicon nitride membrane geometry, where the microheater is embedded within the membrane. In addition to being a robust heating element, the polysilicon microheaters fabricated in this work have a modest and linear thermal coefficient of resistance.

Figure 2a shows a real-color optical image of a 3.5 mm by 3.5 mm chip containing four microheater sensors. Each microheater device has four electrical contacts: two for the microheater leads (source and drain) and two for optional electrical probing of the sensing layer (not used in this embodiment of the platform). Figure 2b shows a zoomed-in view of a single microheater device showing the polysilicon heater (p-Si, orange), the silicon nitride membrane (Si_3N_4 , green) and the platinum sensor leads (Pt, yellow, not used in this work). Figure 2c shows the resistance of a microheater versus dissipated power from Joule heating. Typical room

temperature resistances of the microheaters are $1.6 \text{ k}\Omega \pm 10\%$. The resistance shows a linear relationship with dissipated power with a slope of $\sim 8 \text{ }\Omega/\text{mW}$. To estimate the temperature for a given power, the microheater is heated until there is a faint orange-red color that is detectable by the human eye. Using reported sensitivity of the human eye (~ 100 photons/second [23]) and geometrical considerations, we estimate this temperature to be approximately $700 \text{ }^\circ\text{C}$. Fitting the emitted spectrum to a Planck distribution corroborates this estimation giving a temperature of $682 \text{ }^\circ\text{C}$. Further details on the relationship between the microheater temperature and power will be reported elsewhere.

The dissipated power necessary to bring the microheater to $700 \text{ }^\circ\text{C}$ is $25 \text{ mW} \pm 10\%$. In this temperature range, the heat lost to radiation is negligible ($\ll 1 \text{ mW}$), so the temperature difference between the microheater and the surrounding air is linearly proportional to the dissipated power. Therefore, the effective thermal coefficient of resistance (TCR) of these highly doped polysilicon microheaters is approximately 180 ppm/K . This TCR is exploited to probe the temperature of the microheater-based sensor during operation. The heat generated as hydrogen is catalytically oxidized on the surface of the sensor increases the microheater temperature, which is detected by the change in the microheater resistance.

To incorporate this microheater device into a catalytic combustion sensor, it must be mated with an appropriate catalyst material. Graphene aerogel (Figure 3a) is chosen as the catalyst support since it provides a high surface area ($>1000 \text{ m}^2/\text{g}$) [16] onto which a catalyst material can be deposited, a high specific thermal conductivity ($\sim 5000 \text{ W/m-K}$ in-plane for graphene [24]) to efficiently transfer heat to the microheater, and is stable below $500 \text{ }^\circ\text{C}$ [25] enabling high temperature operation. Platinum nanoparticles are chosen as the catalyst material, due to their well-established catalytic properties, high surface area, and use in nanomaterials-based hydrogen sensors [26,27]. Embedding platinum nanoparticles into the graphene aerogel provides a highly catalytically active material, which can transfer heat with minimal additional mass and is stable at elevated temperatures.

Figure 3b shows a TEM image of graphene aerogel that has been loaded with platinum nanoparticles (Pt NP). The average nanoparticle size is $6.3 \text{ nm} \pm 3.3 \text{ nm}$, as determined by analysis of several TEM images. The Pt NPs are crystalline, as shown in the inset of Figure 3b, and display a lattice spacing of $2.25 \text{ \AA}$, consistent with the Pt(111) crystal planes. Figure 3c shows an SEM image of the Pt NP-loaded graphene aerogel confirming a uniform loading of platinum nanoparticles throughout the material. Energy dispersive x-ray spectroscopy confirms that only carbon and Pt are present, as shown in Figure 3d.

The Pt NP-loaded graphene aerogel is deposited onto the microheater device to complete the fabrication of the catalytic hydrogen sensor and it is placed into the gas sensing setup for testing. The sensor is exposed to hydrogen concentrations between 0 and $20,000 \text{ ppm}$ during which the temperature of the microheater is ramped between 25 and $430 \text{ }^\circ\text{C}$. This is accomplished by applying a 9-level voltage pulse sequence with 500 ms at each voltage ranging from 0.1 to 5.2 V . When the Pt NP-loaded graphene aerogel is heated in the presence of hydrogen, the hydrogen that is adsorbed on the Pt-NPs reacts with adsorbed oxygen to form water and heat. The heat generated from catalytically combusting the hydrogen causes the

temperature of the microheater to increase. This increase in temperature causes an increase in the microheater resistance.

Figure 4 shows the resistance of the microheater (blue, solid line) at a particular temperature level in the pulse sequence versus time as the sensor is exposed to various concentrations of hydrogen (black, dashed line). While data are collected for all 9 voltage levels, only the 15 mW (430 °C) data set is shown for clarity. A stable, reproducible response to hydrogen is observed during exposure to hydrogen during the 70-minute test.

To determine the optimum operation temperature, the sensor response, i.e. $\Delta R/R_0$, is analyzed as a function of input power for the various hydrogen concentrations. Figure 5 shows the average sensor response to 5,000 ppm hydrogen versus power for all nine voltage levels in the pulse sequence. The sensor response increases with increasing heater power, and then plateaus above 11 mW (320 °C). Similar results are seen at other hydrogen concentrations, up to 20,000 ppm. Since there is no benefit to increasing the temperature above 320 °C, further sensor characterization presented here is performed at 11 mW (320 °C).

Maintaining the sensor at 11 mW not only decreases power consumption, but also improves catalyst support lifetime. Graphene has been shown to be stable up to 500 °C [25]. During exposure to high concentrations of hydrogen, i.e. up to 20,000 ppm, the resistance of the microheater can change by up to 4%, which would correspond to an increase of over 200 °C. Therefore, by operating the sensor at a baseline temperature of 320 °C, exposure of the sensor to temperatures above 500 °C can be minimized and the catalyst lifetime prolonged.

Figure 6 shows the response of a microheater sensor that has been functionalized with the Pt NP-loaded graphene aerogel (blue, triangles) and with a bare graphene aerogel (burgundy, diamonds). The response of the Pt NP-loaded graphene aerogel sensor shows a nearly linear, positive dependence on hydrogen concentration, whereas the bare graphene aerogel sensor shows only a slight negative response. This negative response is due to the increase in thermal conductivity of the hydrogen-containing flow stream, which causes the temperature of the microheater to decrease. Pt NP-loaded devices show a similar response when tested in inert environments (See Supplementary Figure S2). This increase in thermal conductivity of the surrounding gas is also evident in the Pt NP-loaded sensor in Figure 6, where at higher H₂ concentrations the response deviates below the expected extrapolation from lower concentrations, as shown by the solid line that is fit to the first 4 data points in Figure 6. Implementation of this sensor in a Wheatstone bridge configuration would compensate for this deviation from linearity.

In addition to sensitivity, response time and recovery time are critical metrics for hydrogen sensing. For applications where leak detection is critical for safety, especially hydrogen generation or storage in indoor spaces, a sensor response time of ~1 s is required.[1] Figure 7 shows the response and recovery of the sensor operating in continuous heating mode at 11 mW (320 °C) for a hydrogen exposure of 20,000 ppm. The response and recovery times to 90% of their steady-state value (t_{90}) are 0.98 s and 0.72 s, respectively. When the sensors are operated in voltage pulsing mode, there is no measureable effect on sensor response or recovery

time, as it responds and recovers in one to two data points (1-2 seconds, see Supplementary Figure S1).

The microheater sensors functionalized with Pt NP-loaded graphene aerogel catalyst are also tested for selectivity. A common interfering gases for hydrogen sensing is methane. Sensitivity to methane is tested for a range of concentrations up to 20,000 ppm. Figure 8 shows the sensor response versus concentration of methane (green, diamonds) and hydrogen (blue, triangles) while heated to 11 mW. There is no measurable response to methane at this power. In fact, detection of methane was not observed even up to 15 mW (430 °C). This likely indicates that either this catalyst is not capable of catalytically combusting methane or that it requires a higher temperature, in which case an alternative catalyst support with higher thermal stability, such as boron-nitride aerogel,[28] would be required.

The selectivity of the catalyst to hydrogen was also tested using two hydrocarbons with low auto-ignition temperatures, namely diethylether (160 °C) and n-pentane: (260 °C). Figure 9 shows the sensor response to 5,000 ppm of these two gases at 320 °C and 430 °C. At 320 °C, the response is extremely small (equivalent to <100 ppm of hydrogen). At 430 °C, the sensor response is significantly larger, but still only equivalent to approximately 800 ppm hydrogen. Complete combustion of these hydrocarbons would release more heat per mole than hydrogen, so the small signal obtained shows that Pt nanoparticles cannot effectively catalyze the combustion in this temperature range. In addition, even though the microheater is heated above the auto-ignition temperature of both gases, the small thermal mass of the microheater prevents significant auto-ignition. Other groups have noted that this feature in microheater-based combustible gas sensors may eliminate the need for bulky, expensive explosion-proof housing, which limit sensor miniaturization and adversely affect sensor response times [29]. The improved selectivity at 320 °C is an added justification for the optimized sensor operating temperature.

Using a low duty cycle heat pulse measurement, where the sensor is heated for only part of the time, decreases the power consumption significantly. To ensure that this pulsing of the heater does not affect the sensitivity of the sensor, the response measured when pulsing the heater is compared to the response when continuously heating the sensor. Figure 10 shows the response of the sensor versus hydrogen concentration when heated to 320 °C for 500 ms every 2.5 seconds (blue squares) and when heated continuously at 320 °C. The response difference between pulsed and continuous mode at any concentration is <10%, and the overall linear calibration differs by only 2%. Meanwhile, the power consumption drops 80% from 11 mW to 2.2 mW. For the pulsed heating mode, the sensitivity determined from a linear fit of the data in Figure 9 is 1.6%/10,000 ppm hydrogen. This corresponds to a sensitivity of 17 mV/10,000 ppm hydrogen if operated in a Wheatstone bridge configuration with a reference sensor with resistance R_0 . This is comparable to many of the commercially available sensors [15] with approximately 100 times lower power consumption. In addition, over a ten-day testing period with over 60 hours of testing, the sensor displayed good reproducibility with an average change in resistance ($\Delta R/R_0$) of 0.015 +/- 0.0015 during exposure to 10,000 ppm hydrogen.

Finally, the limit of detection of the Pt-NP loaded graphene aerogel-based sensors was determined. Figure 11 shows the sensor response to 500 ppm of hydrogen while operating in

pulsed heating mode (500 ms at 320 °C every 2.5 s). The sensor response to 500 ppm of hydrogen is easily distinguishable with a signal to noise ratio of 20:1. As mentioned previously, although the sensor is only heated for a fraction of the time, the response time is approximately the same as the continuously heated sensor (within one data point, data collected every 2.5 s). Concentrations lower than 500 ppm were not tested, due to dilution accuracy of the gas delivery system. However, using a signal to noise threshold of 3, the sensor should be able to detect hydrogen down to 65 ppm.

4. Conclusion

A low power catalytic hydrogen gas sensor has been developed using a micro-machined polysilicon heater functionalized with Pt nanoparticle-loaded graphene aerogel as the catalyst material. The graphene aerogel provides a high surface area for platinum nanoparticle loading and high thermal conductivity for efficient transfer of heat generated from the catalytic combustion of hydrogen. The Pt-NP loaded graphene aerogel are characterized using TEM, SEM, and EDAX confirming the homogeneous distribution of small (~6 nm) Pt nanoparticles within the graphene aerogel. The operation temperature of the sensors is optimized for sensitivity, stability, and selectivity. Using a low duty cycle heat pulse measurement, the power of the microheater functionalized with Pt NP-loaded graphene aerogel consumes as low as 2.2 mW of power without compromising the sensor performance. The sensors have a sensitivity of 1.6%/10,000 ppm hydrogen with a t_{90} response and recovery time of 0.97 s and 0.72 s, respectively. The sensor shows negligible cross sensitivity to other flammable gases, including methane, n-pentane, and diethylether. A lower detection limit of approximately 65 ppm is estimated.

Further investigations into various catalyst materials to tune selectivity and utilization of catalyst supports with higher thermal stability, such as BN aerogel [28], should result in detection of other flammable gases, such as methane. Using the low power microheater platform reported here functionalized with various catalysts and supports, a multi-analyte detection chip can be produced with a very small footprint, thereby enabling wireless battery powered gas detectors at minimal cost for industrial and consumer applications.

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Figure Captions:

Figure 1. Schematic of the fabricated microheater device. (a) Top view of microheater (b) Cross-sectional schematic of the microheater.

Figure 2. (a) Optical image of a 3.5 mm by 3.5 mm chip containing four microheaters. (b) Zoom-in of one microheater. Scale bar: 50 μm . Labels: Polysilicon (p-Si, orange), silicon nitride membrane (Si_3N_4 , green), Pt sensing leads (Pt, gold), silicon nitride on silicon substrate (Si, red) (c) Typical microheater resistance at different applied power values, showing a good linear correlation. Since the power is directly proportional to temperature, there is also a linear correlation between heater resistance and temperature.

Figure 3. (a) TEM image of graphene aerogel prior to loading with platinum nanoparticles. (b) TEM image of Pt nanoparticles dispersed on the graphene aerogel. Dark nanoparticles are supported on the lower-contrast nanoporous graphitic structure. (b, inset) TEM showing Pt (111) spacing of 2.25 $\text{\AA}$. (c) SEM shows Pt loading over a large area, including some larger clusters. (d) EDAX spectrum confirming carbon and platinum are the only elements present. Scale bars: (a,b) 20 nm; (c) 5 μm

Figure 4. Resistance of the sensor (blue, solid line) for varying hydrogen concentration (black, dashed line) versus time for the 15 mW (430 $^{\circ}\text{C}$) level of the nine-level pulse sequence.

Figure 5. Relative sensor response ($\Delta R/R_0$) versus microheater power for 5,000 ppm hydrogen exposure. The error bars represent the standard deviation of the response over the duration of the test.

Figure 6: Relative response ($\Delta R/R_0$) of the microheater-based sensor versus hydrogen concentration functionalized with Pt-loaded graphene aerogel (blue, triangles) and bare graphene aerogel (burgundy, diamonds). Error bars are standard deviation of response during 45 minutes of exposure at selected concentration and if error bars are not seen, they are within the symbol. The microheater is at 11 mW (320 $^{\circ}\text{C}$). The solid line is fit to the first four data points in the plot and acts as a guide to the eye to show the deviation from linearity at high concentrations, due to the increase in the thermal conductivity of the gas stream.

Figure 7. Sensor response to (left) and recovery from (right) exposure to 20,000 ppm hydrogen. Microheater is powered continuously at 11 mW and data is collected every 150 ms.

Figure 8. Response to methane (green, diamonds) at several concentrations compared to response to hydrogen (blue, triangles). Microheater is at 11 mW (320 $^{\circ}\text{C}$). Error bars are standard deviation of response of the fifteen 3-minutes exposures at that concentration and if error bars are not seen, they are within the symbol.

Figure 9. Average relative sensor response to 3,000 ppm of diethylether and n-pentane at 320 $^{\circ}\text{C}$ (red circles) and 430 $^{\circ}\text{C}$ (blue squares). Error bars are the standard deviation of sensor response during 30 minutes of exposure.

Figure 10. Relative sensor response versus hydrogen concentration for pulsed (green diamonds) and continuous (blue squares) modes. Error bars are standard deviation of all data points taken at a given hydrogen concentration during a 3 hour test. Continuous heating is to 11 mW (320 °C) and pulsed heating is 500 ms at 11 mW (320 °C) every 2.5 s.

Figure 11. Sensor response (solid burgundy line) versus time during a 500 ppm hydrogen exposure (dashed black line). Microheater is pulsed for 500 ms at 11 mW (320 °C) every 2.5 s.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

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