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.

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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.

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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 and 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 Fig. 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 °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 h 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 mm × 3.5 mm 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 and 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 though pyrolysis at 1050 °C under nitrogen [16,17]. To decorate with Pt nanoparticles, the graphene aerogels are submerged in an aqueous solution of 0.5 M 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 h 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 cm^3. 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 N_2,), n-pentane (Praxair, 5000 ppm in N_2,), and methane (Praxair, 5% in N_2,) 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 steam 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 $(R - R_0)/R_0$, where R is the average resistance during exposure to given hydrogen concentration and R_0 is the average resistance during zero hydrogen exposure.

3. Results and 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