LOW POWER MICROHEATER-BASED COMBUSTIBLE GAS SENSOR WITH GRAPHENE AEROGEL CATALYST SUPPORT

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ABSTRACT

This paper reports a microheater-based combustible gas sensor with ultra-low power consumption (1.4 mW) using pulsed heating and novel sensing materials. High surface area graphene aerogel is used as a support for platinum and palladium nanoparticles. Pulsed heating (450 °C) at a 10% duty cycle yields an order of magnitude reduction in power consumption with no loss of sensitivity. Sensing response to hydrogen and propane gas shows promising selectivity and order of magnitude faster response and recovery times (1-2 s) compared to previous work. The results indicate a high level of flexibility in creating selective, low power combustible gas sensors using this microheater platform and catalytic material system.

KEYWORDS

Combustible gas sensing, microheater, graphene aerogel, platinum nanoparticles, palladium nanoparticles

INTRODUCTION

Sensing combustible gases is critical for hydrogen and hydrocarbon leak detection, industrial safety, and environmental monitoring. Combustible gas sensors detect a temperature change caused by surface-catalyzed combustion of the target gas. To promote combustion, the catalyst material must be heated to high temperatures (>450 °C), which typically requires power consumption of 500 mW or more [1]. This severely limits the ability for these sensors to be battery-powered.

Microfabricated combustible gas sensors have been developed to lower the power consumption required for heating [2]. Power minimization has largely been achieved through thermal isolation of the heater element, either through backside etching or sacrificial layer etching [3]. Microheater materials are typically platinum or polysilicon encapsulated in low-stress silicon nitride. Our designed platform uses a doped polysilicon microheater. Because polysilicon has higher resistivity than platinum, the heated area can be minimized without electro-migration issues. Shrinking the size allows for our microheater platform to reach 450 °C with only 14 mW. Additionally, the fast thermal response time of the heater allows for rapid duty cycling that lower the power consumption even further.

Progress in microheater development has revealed the need for novel catalytic materials tailored for the microfabricated sensors. Typical catalyst materials have been the same noble metal nanoparticles on porous oxides used in commercial devices. These have poor thermal conductivity and gas diffusion leading to slow response [2,4,5], as well as issues with integration and adhesion on the microheaters [4]. Some researchers have looked to thin films, which can be better integrated into sensor manufacture, but the lower surface area leads to poor sensitivity [4,6]. Use of graphene aerogel (GA) with high surface area and high thermal conductivity as a support for catalytic nanoparticles is an attractive approach that maintains high surface area of catalyst for good sensitivity, and improves response and recovery time [7,8]. Prior work using platinum nanoparticles on graphene aerogel for hydrogen sensing has shown fast response and recovery (<1 s), which is attributed to minimized support mass and improved thermal conductivity of the support [8].

In this paper, platinum and palladium nanoparticles on high surface area GA (approx. 900 m²/g) are investigated as catalytic materials for both hydrogen and propane sensing. Figure 1 shows the catalytic material integrated on the microheater platform.

Figure 1: Sensor schematic. Hydrogen or propane gas reacts on the catalyst nanoparticle surface and releases heat, causing increased temperature of the polysilicon trace, resulting in a resistance increase.

Response and recovery times are within 1-2 seconds for the various metal-gas combinations. The fast response time of both the microheater and the catalyst material open up the possibility of fast temperature scanning to build in selectivity or duty cycling to decrease power consumption.
even further. No loss of sensitivity is seen for the propane response of platinum nanoparticle-loaded graphene aerogel even with 10% duty cycling, which corresponds to power consumption of only 1.4 mW. Using the graphene aerogel catalyst support can unlock the real performance enhancements of microfabricated heaters and enable truly low power combustible gas sensing.

FABRICATION

Microheater Fabrication

The low power microheater platform takes advantage of standard micromachining processes. Figure 2 outlines the fabrication process. A silicon wafer is first deposited with 100 nm of silicon-rich low-stress nitride (LSN) using low pressure chemical vapor deposition, followed by 100 nm of boron-doped polysilicon. The wafers are heated to 1050 °C for film stress release and annealing. Then, the doped polysilicon is patterned with photolithography and plasma etching to form the microheater. Another silicon nitride layer is deposited and patterned to open windows for microheater contact formation. Next, the 10/90 nm thick titanium/platinum layer is deposited and patterned through lift-off to form the contacts and wirebond pads. The titanium layer is used as an adhesion layer between the substrate and platinum. The wafers are then annealed in a nitrogen environment at 350 °C for 1 hour to release Pt film stress. Following this, a protective coating is spun on the front-side of the wafer and the back-side of the wafer is patterned and etched to expose the silicon substrate, which is etched in KOH to isolate the microheaters in a thin silicon-nitride membrane.

Nanoparticle-decorated Aerogel Synthesis

Graphene aerogel synthesis is detailed in Ref. [7]. Briefly, graphene oxide sheets are added to water and ammonium hydroxide and heated at 85 °C to promote gelation. The scaffold is dried with a critical point dryer to retain the pores and pyrolyzed under nitrogen at high temperature to reduce the oxygen-containing groups. Platinum nanoparticle loading follows the process detailed in Ref. [8], where the aerogel is soaked in a 0.5 M aqueous solution of chloroplatinic acid (H₂PtCl₆), freeze-dried, and thermally reduced under hydrogen flow at 450 °C to form pure metallic nanoparticles. Palladium nanoparticle loading is similar, but with palladium chloride (PdCl₂) as the precursor and a solution concentration of 0.1 M.

Sensor Fabrication and Testing

Nanoparticle-loaded graphene aerogel is suspended in water and drop-cast onto the microheater to form the sensor. Fabricated sensors are wirebonded into a cer-dip package and placed in a 1 cm³ gas chamber. Gas flow is controlled with mass flow controllers (Bronkhurst) and Labview. Sensor measurements are performed with a Keithley 2602 sourcemeter. Hydrogen and propane gas tanks are 5% (50,000 ppm) balanced in nitrogen. Hydrogen gas is diluted with dry, clean air to reach the concentrations tested, while propane gas is mixed with nitrogen and oxygen to maintain an oxygen concentration of 20% (Ref. [8] shows no hydrogen response dependence on the percentage of oxygen in the range of 10-21%).

RESULTS AND DISCUSSION

Material Characterization

The graphene aerogel has a specific surface area of 900 m²/g [7], which is much higher than typical values for porous alumina (~100 m²/g) [10]. The thermal conductivity of the graphene aerogel, which is composed of cross-linked few layer graphene sheets, is also several orders of magnitude higher than that of alumina (~1000 W mK⁻¹ for few layer graphene [11] vs. ~10 W mK⁻¹ for alumina [12]). Successful loading of Pt and Pd nanoparticles is confirmed with X-ray photoelectron spectroscopy (Figure 3a and 3b) as well as transmission electron microscopy (Figure 3c and 3d). For the Pt nanoparticles, about 70% have a 1-2 nm radius, with the rest up to 10 nm radius. For the Pd nanoparticles the distribution is tighter, with about 70% at a 1-2 nm radius and the rest larger, up to 5 nm. The density of Pd nanoparticles is lower because a lower concentration of the metal salt was used. The Pt lattice spacing of 2.28 Å is consistent with the Pt(111) crystal plane, and the Pd lattice spacing of 2.22 Å is consistent with the Pd(111) crystal plane (insets of Figure 3c and 3d respectively).

Sensing Response

Sensitivity is defined as R-Rₒ/Rₒ x 100% where R is the average resistance during a given exposure and Rₒ is the average resistance with 0 ppm concentration. Figure 4 shows the result of hydrogen and propane exposure to the Pt...
nanoparticle-loaded GA sensor (Pt-GA) and Pd nanoparticle-loaded GA sensor (Pd-GA) at optimum response temperature for each metal-gas combination. Hydrogen sensitivity is greatest at a temperature of 325 °C for Pt-GA, while for Pd-GA, sensitivity peaks at 400 °C. The peak in response corresponds to a shift from a kinetically-controlled regime to a mass transfer-limited regime. Further increases in temperature in this regime may decrease sensitivity by making gas adsorption less favorable. For propane, there is no response for Pt-GA below 400 °C, but the graphene aerogel has limited stability at high temperature, thus 450 °C is chosen as a balance between sensitivity and thermal stability. Pd-GA shows no response to propane even up to 550 °C (450 °C is shown in Figure 4). The observed differences in response between Pt-GA and Pd-GA may arise from differences in catalyst loading and inherent different in interaction between the metal and the gas. With our microheater platform, the maximum power consumption is 14 mW (to reach 450 °C). Given the sensor response towards different gases varies with both temperature and catalyst material (Pt vs. Pd), a selective combustible gas sensor array can be constructed.

The fast response and recovery also enable duty cycling with no loss of sensitivity. For example, the Pt-GA sensor was tested for propane response with continuous heating at 450 °C and with a 10% duty cycle (heating to 450 °C for 100 ms every second, with the sensor at room temperature in between). Figure 5c shows comparable sensitivity between the continuous heating and pulsed heating case and Figure 5d shows the response time during pulsed heating is slightly longer, but still within a few seconds. With this strategy, power requirements are in the single mW range.

Prior work for hydrocarbon sensing on porous alumina catalyst supports shows response times on the order of 20 s [5, 13]. Response and recovery times for Pt-GA exposure to propane and Pd-GA exposure to hydrogen are shown in Figure 5a and 5b and are seen to be fast in both cases (within 1-2 s). The high thermal conductivity of the graphene aerogel may allow for faster transfer of combustion heat to the sensor. Also, the high specific surface area means less support material is used for the same platinum loading, minimizing the power needed for heating the support.
Although the graphene aerogel has great benefits in sensor response and recovery and power consumption, the stability is poor at the higher temperatures needed for propane sensing. Besides requiring higher heater temperatures, propane combustion releases more heat than hydrogen and can significantly raise the temperature of the sensing material. When the Pt-GA was exposed to 2% propane with the microheater initially at 450 °C, the temperature is estimated to increase to 725 °C, which is above the stability point. Visible loss of material is observed (Figure 6), although the sensing response does not completely disappear. In order to combat the thermal instability, future work will investigate boron nitride aerogel as a support material. Boron nitride aerogel has lower specific surface area than graphene (450 m²/g), but thermal stability up to 800 °C in air [14].

![Figure 6: Optical images of Pt-GA on the microheater (a) before testing; (b) after several hours of propane testing with microheater at 450 °C.](image)

CONCLUSIONS

A combination of low power microheater and improved catalyst support opens possibilities for low power and selective combustible gas sensing. The high specific surface area graphene aerogel allows for high loading of catalyst nanoparticles while improving the response and recovery time for both hydrogen and propane gas to 1-2 s. The fast response of the microheater and the catalyst support means pulsed heating can be used to lower the power consumption to the single mW range without losing sensitivity (1.4 mW for 10% duty cycling of Pt-GA response to propane). Selectivity can be built in at low power by rapidly scanning temperatures or creating an array with different materials on adjacent microheaters. Instability with the graphene aerogel at high temperature suggests boron nitride aerogel as a support material that retains the advantages of high surface area and thermal conductivity, while giving improved thermal stability.

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