Final Technical Report

on

The Development of a Solid-State Hydrogen Sensor for Rocket Engine Leakage Detection

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Submitted by

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Introduction

Hydrogen propellant leakage poses significant operational problems in the rocket propulsion industry as well as for space exploratory applications. Vigorous efforts have been devoted to minimizing hydrogen leakage in assembly, test and launch operations related to hydrogen propellant. The objective has been to reduce the operational cost of assembling and maintaining hydrogen delivery systems. Specifically, efforts have been made to develop a hydrogen leak detection system for point-contact measurement.

Under the auspices of Lewis Research Center, NASA, Cleveland, Ohio, the Electronics Design Center at Case Western Reserve University, Cleveland, Ohio, has undertaken the development of a point-contact hydrogen gas sensor with potential applications to the hydrogen propellant industry. We envision a sensor array consisting of numbers of discrete hydrogen sensors that can be located in potential leak sites. Silicon-based microfabrication and micromachining techniques are used in the fabrication of these sensor prototypes. Evaluations of the sensor are carried out in-house at Case Western Reserve University as well as at Lewis Research Center, NASA, and GenCorp Aerojet, Sacramento, California.

The hydrogen gas sensor is not only applicable in a hydrogen propulsion system, but also usable in many other civilian and industrial settings. This includes vehicles or facility use, or in the production of hydrogen gas. Dual space and commercial uses of these point-contacted hydrogen sensors are feasible and will directly meet the needs and objectives of NASA as well as various industrial segments.

Fabrication and Characterization of the Hydrogen Sensor

The developing hydrogen sensor is a palladium-silver film gate Schottky diode. This sensor is based on metal-oxide-semiconductor (MOS) technology similar to that used in the semiconductor electronics industry. The gas sensing MOS structure is composed of a hydrogen sensitive metal deposited on an insulator adherent to a semiconductor. This forms a Schottky diode in the case of a very thin layer of the insulator. A Pd-SiO_2-Si structure is a commonly used MOS structure for hydrogen detection. Hydrogen dissociates on the Pd surface and diffuses to the Pd-Si-O_2 interface affecting the electronic properties of a MOS system. The use of pure Pd as the hydrogen sensitive metal can be problematic for several reasons. The most serious one involves a phase change that occurs at high hydrogen concentrations which can lead to a hysteresis effect or embrittlement of the film. Physically, pure palladium is too soft to maintain a well-defined geometric structure. In our development, palladium with 13% silver is used as the gate film material. The palladium-silver film is more resistant to damage from exposure to high hydrogen concentrations than pure palladium. Also, the alloy film shows a faster time response than palladium. The 13% Ag in the palladium is the optimum concentration for balancing these improved properties while maintaining sufficient sensitivity to the hydrogen.

The structure of the fabricated sensor incorporates a temperature detector and a heater. Both the temperature detector and heater are platinum resistance type, and the sensor structure is shown in Figure 1. The sensor is then mounted on either a TO5 header or a ceramic flat-pack structure. The surface area of the Schottky diode is approximately 6.1×10^{-3} cm^2.

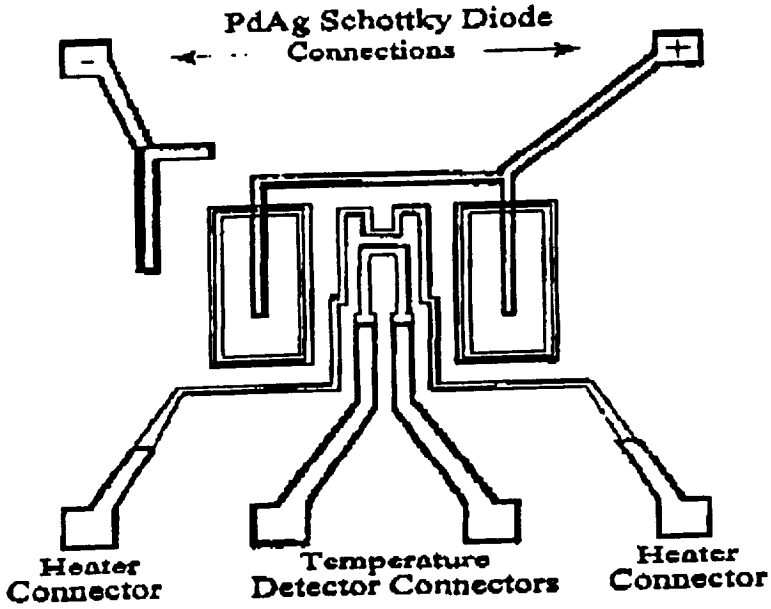

Figure 1: Schematic Structure of the Pd-Ag Schottky Diode Hydrogen Sensor

The characteristics of the sensor were assessed in this study. The electronic properties of the Schottky diode, in a sense, the sensor performance, can be evaluated by measuring the forward voltage at a constant current.

The time response of the sensor was evaluated at Lewis Research Center, NASA, at a temperature of 45°C to hydrogen of 0.2%. Figure 2 shows the actual response. Two different carrier gases were used in this study, pure nitrogen and a mixture of 90% N_2 and 10% O_2. The sensor was first exposed to the carrier gas for 10 minutes, then to 0.2% H_2 in the carrier gas, then to the carrier gas again. Experiments were repeated for at least 4 cycles.

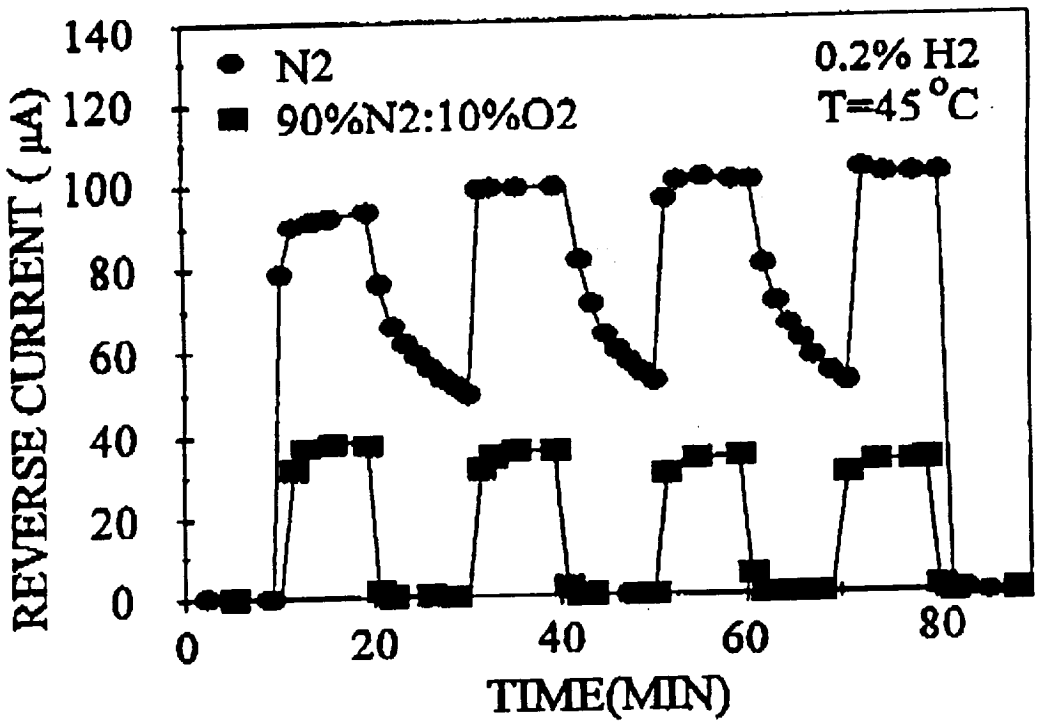

Figure 2: Time Response of the Sensor to Cycling of 0.2% H_2 in N_2 and 90% N_2 and 10% O_2

Several features of the sensor performance should be noted. First the sensor is highly sensitive to hydrogen with a rapid response to hydrogen introduction to either an inert or an oxygen containing carrier gas. For reverse current measurement, the sensor output increases by a factor of 1000 in the presence of hydrogen. The response time to the hydrogen, obviously, depends on the gas flow rate and the size of the testing chamber in order to attain equilibrium. Under the conditions of this study the response time is less than 45 seconds to reach 90% of the steady-state value.

Secondly, the presence of oxygen appears to affect the sensor performance. The presence of oxygen seems to lower the sensor output as well as the baseline recovery time. The recovery time to 90% of the baseline value in a nitrogen and oxygen mixture is on the order of seconds, while the recovery time in pure nitrogen is on the order of a few minutes.

Thirdly, the repeatability of the sensor response appears to be very good. For each exposure to hydrogen, as shown in Figure 2, the reverse currents in repeated measurements are within 13% of the same value. It should be noted that this 13% variation is out of a total change of approximately 1000 for both gas mixtures. Also, the pattern of the slower recovery in nitrogen is repeatable.

The temperature effect on the sensor performance over a hydrogen concentration of 100 to 5000 ppm in a 90% N_2 and 10% O_2 carrier gas was evaluated. The sensor temperatures tested were 45°C, 60°C, 80°C and 100°C. Figure 3 shows the temperature effect on the sensor performance. In the test, the sensor was first exposed to the carrier gas for 10 minutes, then for 10 minutes each to, 100 ppm, 500 ppm, 1000 ppm and 5000 ppm H_2 in the carrier gas. The hydrogen flow was then stopped and the sensor recovered towards the carrier gas. In Figure 3, the sensor response is shown on a linear scale, while the inset shows the first 30 minutes of the same test on a logarithmic scale.

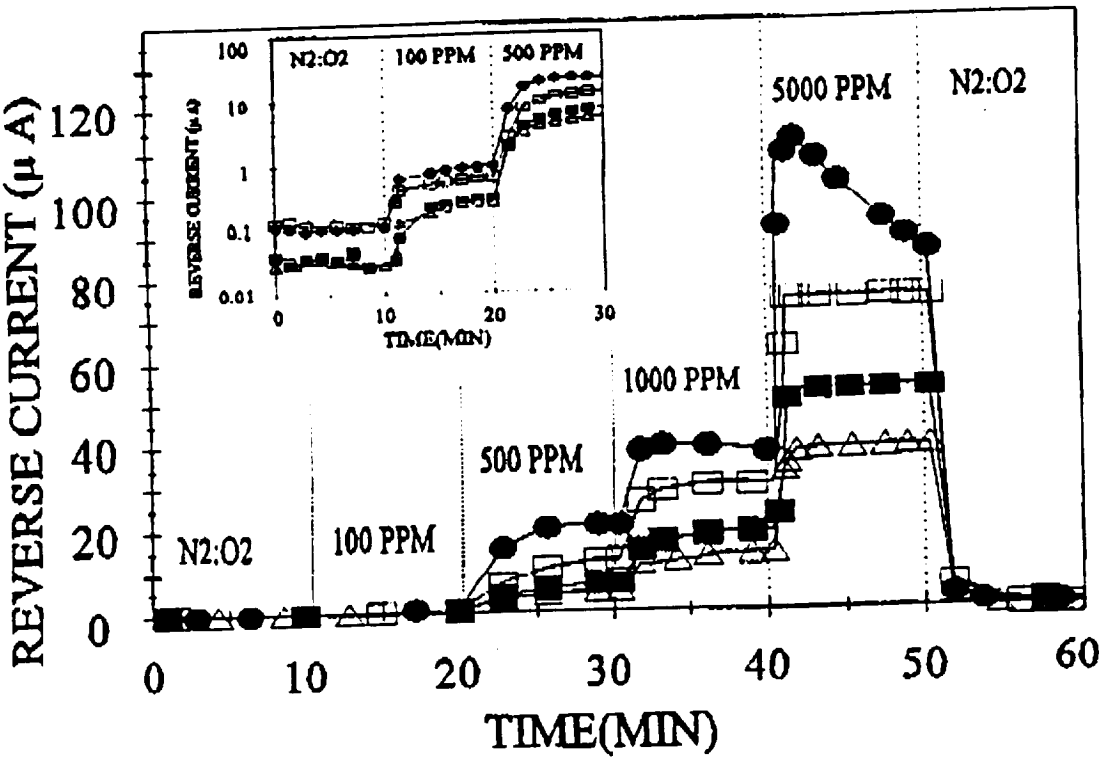

Figure 3: Sensor response as a function of temperature when exposed for 10 minutes to the carrier gas 90% N_2: 10% O_2, and then for 10 minutes each to 100, 500, 1000, and 5000 ppm of H_2 in the carrier gas. The inset shows the carrier gas, 100 and 500 ppm in a logarithmic scale. The temperatures are 45°C (Δ), 60°C (■), 80°C (□), and 100°C (●)

The magnitude of the response and the time it takes for the sensor to reach a stable value is temperature dependent. The higher the temperature, the larger the reverse current and the shorter the time until the reverse current stabilizes. The reverse current reaches a maximum almost immediately upon the hydrogen concentration from 1000 ppm to 5000 ppm. This high concentration/high temperature behavior of the sensor is being assessed by other investigators, which we plan to do in future research.

With the testing results thus far, the 13% Ag-palladium hydrogen sensor can be very useful in sensing low levels of hydrogen, namely at the ppm level.

In summary, the palladium-silver hydrogen gas sensor can be potentially used for many meaningful applications. With specific focus on propellant and space applications, we plan to overcome the following shortcomings:

1. When the sensor is exposed to a high level of hydrogen, i.e., 100%, the sensor appears to deteriorate irreversibly. This suggests that a resistor structure of the Pd-Ag sensor instead of a Schottky diode may be advantageous. This aspect will be investigated in the future.

2. In addition to palladium-silver film as a gate material, other palladium alloys including palladium-chromium, palladium-nickel, etc., have also been suggested for hydrogen gas sensing gate material for a Schottky diode device. It is planned that future studies involving these or other palladium-alloys for gate film will be carried out.

3. The present hydrogen sensor prototype is fabricated on a silicon wafer. It may be desirable to consider using a substrate which can be used in a high temperature

environment. Silicon carbide, SiC, is one of the prospective materials, and we will investigate the possibility of using SiC for the construction of the device.