Palladium capped samarium thin films as potential hydrogen sensors

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Abstract

We show here that a palladium capped samarium film at room temperature can be used as an efficient sensor material for hydrogen detection. As low as 194 ppm of hydrogen gas can be detected without any cross sensitivity problem. Depending upon the partial pressure of hydrogen, response times varying from 6 to 30 s have been obtained. An interesting observation is very fast hydrogen desorption (2 s) at room temperature, thus making the sensing element ready for reuse quickly. No external source is needed with this sensor element.

Keywords: Palladium; Samarium; Hydrogen sensor; Electrical switching

1. Introduction

Associated with the increasing use of hydrogen in many industries such as chemical, food, metallurgical, electronic and others and its anticipated greater utilization as a source of clean abundant energy, is the issue of its safe storage, transportation and handling. A hydrogen leak should be avoided because hydrogen when mixed with air in the ratio of 4.65-93.9 vol.% is explosive [1]. Highly sensitive hydrogen sensors are therefore needed to detect H2 gas leakage. Critical sensor performance requirements include high selectivity, fast response, insensitivity to other gases, durability and potential for low cost production. Different types of hydrogen sensors have been reported [1-9] and many are commercially available. Detection of hydrogen using bulk rare earth metal hydrides was proposed as far back as 1973, however, the proposed approach was specific to steel industry but not adaptable for other applications [10]. The recent discovery [11] of spectacular changes in optical and electrical properties of thin film rare earth metals upon hydrogenation has triggered large-scale investigations to exploit these materials for various technological applications. While investigating samarium films covered with palladium overlay for their electrical and optical switching behavior, we observed that exposure of these films to hydrogen, leads to a change in electrical resistance that scales with hydrogen concentration in the gas phase. The reaction is reversible suggesting that Pd capped samarium films could be used as hydrogen sensing elements. We show here that it is indeed so and these films demonstrate highly desirable features, such as fast response and recovery speeds, sensitivity to hydrogen in ppm range and absence of cross sensitivity to possible contaminant gases.

2. Experimental

Samarium films of thickness 55 nm were deposited by vacuum evaporation on a 15 mm x 15 mm x 2 mm ultrasonically cleaned glass substrate, two edges each 2 mm x 2 mm of which were precoated with aluminum and bonded with copper wire for taking electrical contacts. The chamber was repeatedly purged with high purity Argon gas for about 30 min and then evacuated. The pressure in the chamber was 1 x 10^-6 Pa prior to deposition. A continuous Pd overlay of thickness 12 nm was then deposited over the Sm film (except in the region above contact B where the thickness was restricted to 3.5 nm) without breaking the vacuum. The configuration is shown in Fig. 1. The palladium
overlayer provides protection to the underlying film against oxidation, increases the hydrogen sticking coefficient and acts as a catalytic layer, which assists in dissociative absorption and associative desorption of hydrogen molecules at reasonably high rates. The diffusion coefficient of hydrogen in palladium is $3 \times 10^{-9} \text{cm}^2\text{s}^{-1}$ [12] at room temperature. Hydrogen in monoatomic forms only reacts with Sm at room temperature. Since the Pd overlayer remains metallic even after hydrogenation, 12 nm electrically continuous Pd layer, if used over the entire surface area of samarium film, masks the observation of a metal to semiconductor transition because the Pd film provides a low resistance path to the applied current. (It may be noted that the resistance of a 12 nm Pd film on 15 mm x 15 mm x 2 mm glass substrate is 615 Ω, whereas that of a 3.5 nm Pd film is 700 kΩ). The Pd capped Sm film (Pd-Sm) was used as a sensing element for detection of hydrogen. The sensing element was housed in a sample holder containing air at normal pressure and at room temperature. Controlled quantity of hydrogen or other gases could be introduced into the specimen holder using mass flow controllers. The specimen holder also had a provision for monitoring resistance of the sensor element. The resistance was measured by two probe method using electrometer (Keithley, Model 6517A). By opening the upper lid of the sample holder, the sensing element could be fully exposed to atmosphere.

3. Results and discussions

The reaction of samarium with hydrogen proceeds as follows:

$$\text{Sm} + 32\text{H}_2 \rightarrow \text{SmH}_2 + \frac{1}{2}\text{H}_2 \text{ at SmH}_3$$

The second step is a reversible transition, which can easily be induced by changing the H$_2$ gas pressure, whereas the first step is essentially unidirectional. This is because of the relative small heat of formation for the second step (-39.6 kJ mol$^{-1}$ H$_2$) compared to the heat of formation for the first step (-202.6 kJ mol$^{-1}$ H$_3$) [13]. The dihydride state is metallic and the trihydride state semiconducting. The transition from the dihydride to trihydride state on absorption of hydrogen is responsible for the metal to semiconductor transition.

Fig. 2 shows the variation of response time $t_r$ required to switch from the metallic to the semiconducting state as a function of hydrogen concentration $c$. $t_r$ is defined as the time required for the initial resistance of Pd-Sm film (60 Ω) to reach 90% of the saturation value of Pd-H0.6-SmH$_3$ (35 kΩ) (0.6 hydrogen atoms are absorbed per Pd atom [14]). The magnified view for hydrogen concentrations from 194 to 10,000 ppm is shown in the inset of the same figure. It is clear that the switching is very fast, the switching time varying from 30 s for 194 ppm of hydrogen to 6 s for 10,000 ppm of hydrogen. The response time of the sensing element (except at a very low hydrogen concentration 97 ppm) decreases exponentially with increase in hydrogen concentration. Once the hydrogen supply to the sensor element is cut off and the lid of specimen holder lifted, the hydrogen incorporated in the sensor element desorbs to the atmosphere within 2 s. The sensing element is then again ready for detection of hydrogen and the process can be repeated over a large number of cycles. This is shown in Figs. 3 and 4 for 10,000 and 194 ppm of H$_2$, respectively. This fast desorption is possible because the desorption process in all rare earth metal hydrides is endothermic [15] and hydrogen has a large diffusion coefficient (0.61 cm$^2$ s$^{-1}$) in air [16]. Since the sensing element is in atmosphere, it appears that it is able to absorb requisite heat from the atmosphere leading to quick desorption of.
hydrogen, a fact substantiated by a slower observed desorption in vacuum as discussed later.

One of the prime concerns in sensors is that the sensor element should not respond to gases other than the one, which it is supposed to detect and monitor. Cross sensitivity to contaminant gases was checked by introducing 10,000 ppm of potential contaminants, like hydrogen sulfide, carbon dioxide, mixture of argon and methane, argon and ethyl alcohol into the specimen holder assembly and the resistance monitored as a function of time. No change in resistance was detected (Fig. 5) suggesting that this sensor element is free from cross-sensitivity problems. We have also checked our sensing element (Pd-5nm) inside a vacuum chamber. When hydrogen gas was introduced inside the chamber (at $4 \times 10^{-10}$ Pa), the response time was found to be almost the same as that in air (Fig. 6). However, the recovery time was found to be much larger even though we used a rotary pump for removing hydrogen absorbed in PdH0.6SmH3 - § film.

It may be pointed out that in general, a sensor element after detection, needs some external source to restore it to its original state e.g. temperature [17], power (8) etc. Neither any temperature control nor any power etc are needed in the original state e.g. temperature [17], power (8) etc. Neither any temperature control nor any power etc are needed in the present case. Further, the problem of water formation does not occur unless the sensing element continues to be exposed to hydrogen for a prolonged period (>6h). However, once water formation takes place, the response time does increase.

Though we have tested our element for 100 cycles, more investigations on its stability are needed, especially in very humid conditions.

In conclusion, we have shown that a palladium capped samarium film exhibits a very high absorption and desorption efficiency for hydrogen at room temperature without any need for an external source. It can detect low concentrations of hydrogen, which makes it a potential base material for hydrogen sensing applications.

References

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