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Hydrogen sensor using optical reflectance from porous silicon with a palladium thin film

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ABSTRACT

Results of a hydrogen sensor based on light scattering from a porous silicon surface coated with a thin palladium film are discussed. Reflected light scattered from the rough surface of porous silicon surface with a thin palladium film is compared before and after exposure to hydrogen gas. After exposure to hydrogen gas the sensor's optical reflectance is decreased indicating the presence of hydrogen.

Keywords: surface roughness, atomic force microscopy, hydrogen sensor, optical sensing.

1. INTRODUCTION

Porous silicon (PSi) can be used as smart transducer material in sensing applications and in the detection of vapors, liquids, and biochemical molecules. Upon exposure to chemical substances, several physical quantities, such as refractive index, photoluminescence, and electrical conductivity, change drastically. A key feature of a physical transducer, being sensitive to organic and biological molecules, either in vapor or liquid state, is a large surface area: PSi has a porous sponge-like structure. PSi is an available, low-cost material, compatible with standard IC processes, which can be employed in the realization of smart sensors and microsystems.

Recently, experimental work has been reported concerning the use of porous silicon in optical sensors for chemical and biological sensing [1]–[5]. In environmental monitoring, optical readout techniques are of particular interest because they do not require electric contacts that may cause explosions or fire in dangerous environments. Also optical sensors are not affected by electromagnetic interference.

Hydrogen gas is expected to play an important role as a clean energy resource. It is essential to develop a sensing device for hydrogen gas because it is explosive over a large range of concentrations with low ignition energy. An optical hydrogen sensor is a possible candidate with good safety characteristics [6].

2. EXPERIMENTAL METHODS

The porous silicon samples are made using [100] p-type silicon wafer with 4 ohm-cm resistivity. The silicon wafer is anodically etched in 15% HF and methanol alcohol solution at a current density of 6 milliamps per square centimeter for 15 minutes.

The samples are analyzed using an XE-100 SPM manufactured by Park Systems (formally PSIA). Images are made of the PSi in the AFM non-contact mode. These SPM images record the topography of the samples surface. The reflected optical spectrum is measured at normal incidence angle using a Filmetrics spectrometer in the reflectance mode. The palladium film thickness is also measusre using a scanning electron microscope (SEM) by JEOL

The palladium thin film is deposited on the porous silicon surface using a Hummer V, DC sputter magnetron deposition system made by Technics. The Hummer deposition systems voltage is set to 4 volts and current to 12 ma for a deposition time of 5 minutes.

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The hydrogen sensors reflectance spectrum is measured before and after exposure to hydrogen gas. All reflectance measurements are done at normal incidence to the surface of the sensor. The sensors exposure to hydrogen is done in a vessel of two percent hydrogen gas and 98 percent nitrogen gas at room temperature and atmospheric pressure for a five minute exposure time. For all tests done in this paper the sensors were exposed to hydrogen gas for five minutes, then the sensors were removed and exposed to air as the optical reflectances are measured.

3. RESULTS AND DISCUSSION

Using an atomic force microscope, images of the surface of the anodically etched porous silicon surface were collected. A typical portion of the porous silicon surface area is shown in Figure 1. Here a 1x1 micron scan is shown. The textured porous silicon surface area has been greatly increased over that for a flat silicon wafer. Red and green colors can be seen reflected off the surface of the porous silicon. These red and green colors are shown as reflection peaks in the reflection spectrum (see Figure 4). Previous research has shown the reflected colors are related to the size of the features on the surface that scatter light [1].

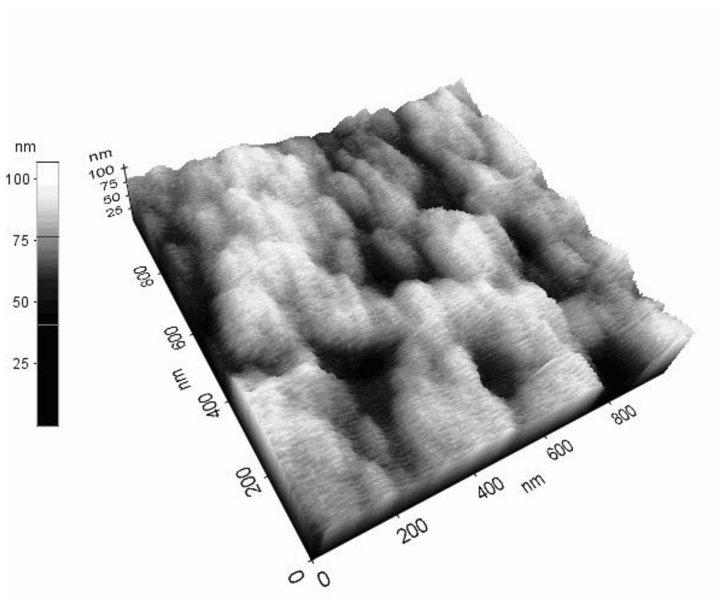
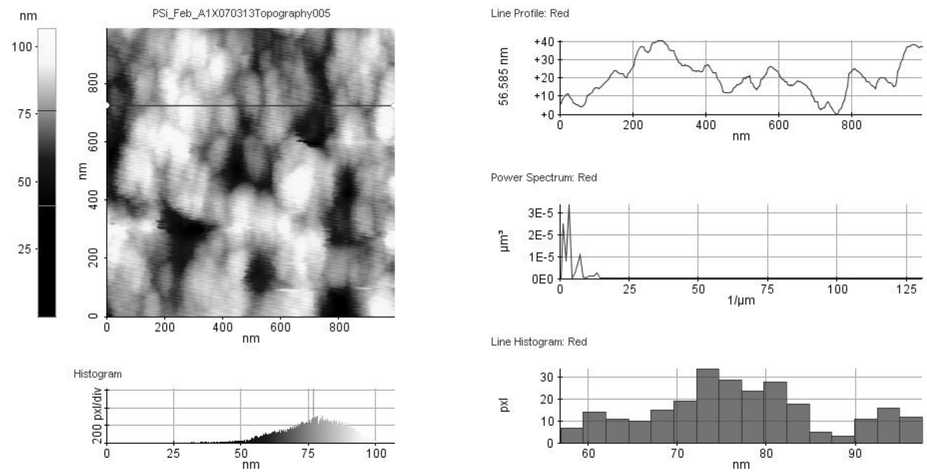


Figure 1. AFM surface image of the porous silicon hydrogen sensor.

From the AFM image a typical line profile across the porous silicon surface is shown in figure2. The right hand side plot shows a cross section of the porous silicon. Here the maximum peak to valley height is 40 nm, also notice the relative size of the bumps of the PSi. The probability distribution function (PDF) of the feature heights is shown in the lower right hand corner for this line profile. The PDF of the height distribution for the entire image is shown in the lower left hand corner of figure 2.



Statistics

Line	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	56.585	97.365	76.975	76.858	40.780	9.919	7.857	0.455	-0.213	2.498

Figure 2. Line profile for the AFM image of the porous silicon surface.

Next, the porous silicon surface is coated with a thin palladium film. The palladium film thickness measured using SEM is approximately 38 nm on flat silicon . Using the optical reflectometer the thickness of the palladium film is measured to be 36 to 44 nm on flat silicon. Finally, using AFM the palladium film was measured to be between 21 and 26 nm on the rough porous silicon surface. An AFM image of this surface is shown in figure 3. Note, the roughness of the underlying porous silicon has greatly increased the effective surface area of the palladium thin film.

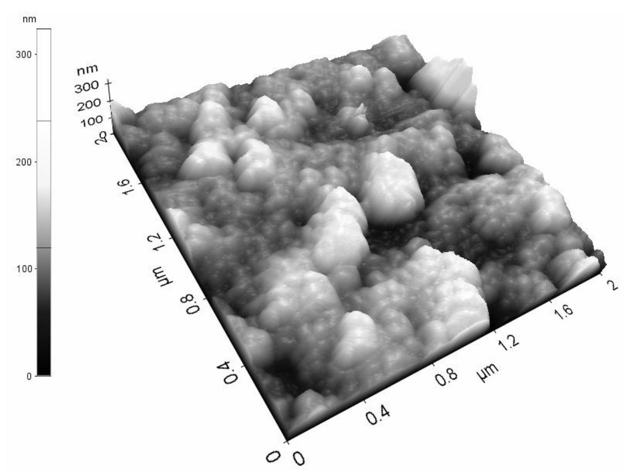


Figure 3. AFM image after palladium thin film deposition onto the surface of porous silicon.

Reflectance measurements are recorded with white light illumination of the surface at a normal incidence angle. The normalized reflectance curve before hydrogen gas exposure is shown as the topmost curve in Figure 4. This curve shows a red colored reflectance peak at 720 nm wavelength and a green colored reflectance peak at a 575 nm wavelength.

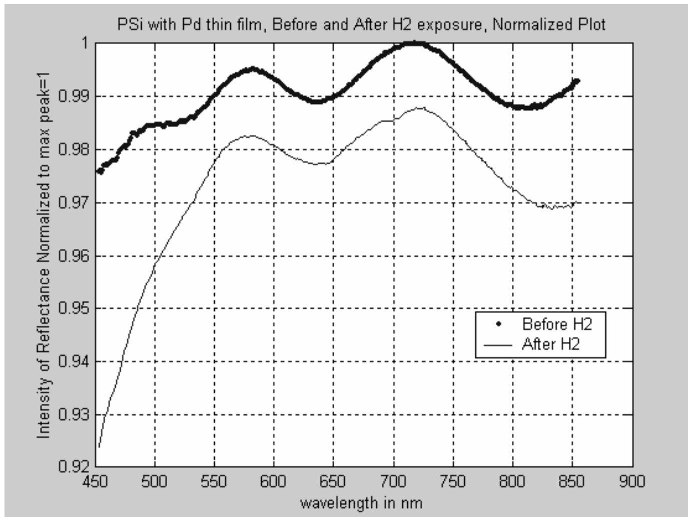


Figure 4. Before and after sensor's exposure to 2% hydrogen gas at atm. pressure
The maximum reflectance peak before H2 exposure is normalized to equal 1.

The reflectance spectrum of the palladium coated porous silicon sensor is measured before and after exposure to hydrogen gas. As a reference, the peak value of the reflectance before hydrogen exposure is normalized to unity and the after exposure curve is scaled by the normalization factor. Figure 4 demonstrates a significant shift in the reflectance before and after hydrogen exposure indicating the presence of hydrogen gas. Notice that this sensor is most sensitive to hydrogen exposure at short (450 nm.) wavelengths, and also to a lesser degree at long (850 nm.) wavelengths.

Figure 5 demonstrates the effects of time after the sensor has been taken out of the hydrogen filled vessel and exposed to air. At successively increasing time measurements in air the sensor's reflectance continues to decrease (see figure 5).

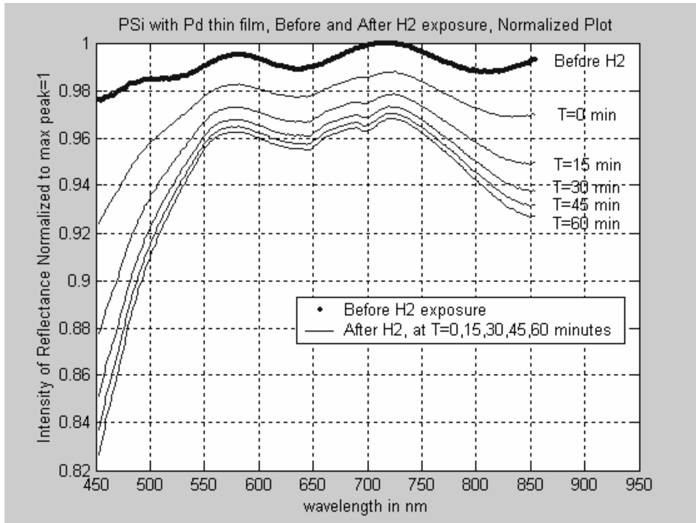


Figure 5. Reflectance for increasing times after hydrogen exposure.

In Figure 5 the sensor is exposed to air starting at time, T = 0, at successively increasing times the reflectance is decreasing.

An interesting result occurs with the palladium covered porous silicon sensor. After a 5 minute exposure to hydrogen the sensor is removed from the hydrogen vessel and expose to air. Reflectance measurements are recorded at time 0, 15, 30, 45, and 60 minutes after hydrogen exposure. The reflectance is changing after removal of the hydrogen to ever decreasing reflectance values. After approximately 72 hours the sensor does finally return to its original before hydrogen exposure state.

A possible explanation for this behavior is the change in surface area due to the rough textured surface of the porous silicon (see Figures 1, 2, and 3). The results seem to indicate that hydrogen is slowly diffusing further and further into the palladium film, even after the initial exposure to the hydrogen gas. After about 36 hours the hydrogen starts to reverse direction and diffuse out of the palladium. Finally, after about 72 hours the sensor is back to its original state with all the hydrogen removed from the palladium film. This effect is similar to a shrunken sponge before water has been added, it expands with water added, and the days later the sponge dries out and shrinks to its original state.

For comparison, another similar hydrogen sensor is tested. This sensor is exactly like the previous sensor except that the palladium film is coated on top of a flat single-sided-polished silicon wafer. This sensor has the same palladium film thickness as the porous silicon sensor. In a similar manner the reflectance of this sensor is measured before and after a 5 minute exposure to hydrogen gas. The reflectance plots are normalized and are shown in figure 6. None of the reflectance peaks associated with the porous silicon exist. However there is a noticeable shift in the reflectance before and after hydrogen exposure (see figure 6).

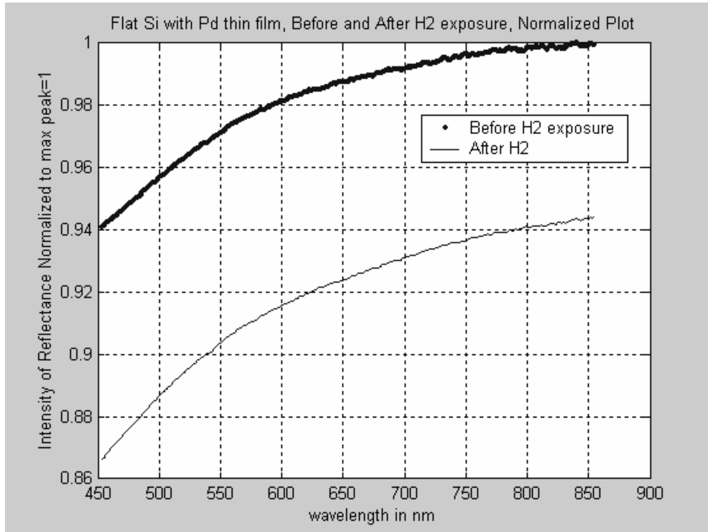


Figure 6.) Flat silicon with a palladium thin film hydrogen sensor.

Next we look at how this flat sensor evolves in time. Figure 7 is an expanded view of Figure 6. The reflectances at time T=0, 20, and 30 minutes after hydrogen exposure are shown. Here, the reflectance after H2 exposure is observed to slowly increase with time as the sensor returns to its original state before hydrogen exposure.

The sensor with the flat surface behaves as expected, with minimum reflectance at time zero and the reflectance returning to its original (before hydrogen exposure) state as time increases. This indicates that after hydrogen exposure, with the sensor exposed to air, the hydrogen immediately starts to escape from the palladium film, and the sensor returns to its original state.

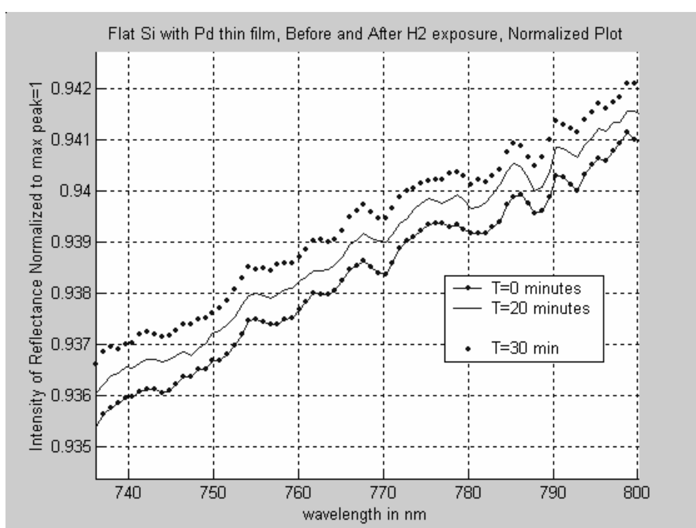


Figure 7. Flat silicon with palladium thin film sensor response after H2 exposure.

4. SUMMARY

The use of a palladium coated porous silicon optical sensor has been demonstrated. This sensor's optical reflectance changes significantly when exposed to hydrogen gas. The sensor is most sensitive at short (450 nm) optical wavelengths. It iss experimentally found that using a textured surface the palladium thin film took several days to recover to its initial state. Whereas the sensor with a flat silicon immediately started to recover to its initial state after the removal of the hydrogen gas. The increased surface area due to the textured porous silicon surface is believed to have a large effect on the results. This is an interesting result and an area for further investigation.

5. ACKNOWLEDGEMENTS

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