Porous Silicon Gas Sensors for Room Temperature Detection of Ammonia and Phosphine

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Nanopore covered microporous porous silicon (PS) interfaces have been formed to provide an active scaffolding for the creation of rapidly responding, reversible, and sensitive, (≤1 ppm) PS gas sensors, operating at room temperature, and based on a uniquely formed highly efficient electrical contract to the nanopore covered microporous array. These sensors are modified on the basis of a general acid-base theory, introducing active nanoparticles to establish gas selectivity. NH<sub>3</sub> and PH<sub>3</sub> have been monitored well below the ppm level.

Introduction

Porous Silicon (PS) has been intensively studied in the last two decades. While its luminescence properties have been considered for optoelectronics, the ability to form a large surface area channel like structure in this material enables a variety of sensor applications. Recently, biochemical (1-3), microfluidic flow (4), temperature and pressure (5), magnetic (6,7), chemical ion (8) and gas sensors have been reported (9). NH<sub>3</sub> and NO<sub>x</sub> for asthmatics and the HCl and PH<sub>3</sub> products of methamphetamine are possible at the 100 ppb levels. Gold coated nanostructures on a PS micro/nanostructured hybrid configuration provide a substantial increase in sensitivity to NH<sub>3</sub>. The hybrid silicon gas sensors further display the advantages of operation at room temperature as well as at a single, readily accessible, temperature with an insensitivity to temperature drift; operation in a heat-sunk configuration with a surface temperature up to 80°C even in highly elevated temperature environments, in sharp contrast to metal oxide sensors; ease of coating with gas-selective materials; low cost of fabrication and operation, and the ability to rapidly assess false positives by operating the sensor in a pulsed mode.

Fabrication and Experiment

Single-crystal (100) boron-doped p-type silicon wafers with resistivities of the order 1-20 Ω-cm have been used to form a hybrid (nanopore covered microporous) structure. The wafers are coated with SiC and, via a Plasma Thermal RIE (Reactive Ion Etcher) openings of 2 to 5 mm rectangles are created on the SiC layer. Gold contacts of approximately 3000 Å thickness are coated with an e-beam evaporator to the ends of the openings using a shadow mask. Hybrid nanopore coated microporous PS samples are fabricated in these openings using an electrochemical cell constructed from high-density polyethylene. A working electrode is attached to the back of the wafer and the counter electrode corresponds to a platinum foil placed in solution. The cell is sealed as the openings on the SiC layer make contact with the etch solution. A magnetic stir-bar is used to prevent the buildup of hydrogen on the silicon surface. The samples are etched in...
a solution of 1M H$_2$O, 1M HF, and 0.1 M tetrabutylammonium perchlorate (TBAP), all in acetonitrile. These hybrid samples are etched with a current density of 3.0 mA/cm$^2$ for 45 minutes as nanopore covered ~ 10 µm deep micropores are created on the surface. A “bright electroless gold” solution from Transene Company is used to coat the basic sensors by immersing the sensor for 20-40 s in the solution. Ammonia and phosphine are diluted in ultra high purity (UHP) nitrogen using computer controlled mass flow controllers. Before the tests, the 1/8” lines carrying this mixture are flushed with UHP N$_2$ for extended periods. All tests are done at near atmospheric pressure and room temperature in an open environment and hood.

**Results and Discussions**

We approach the modification of sensor surface sensitivity for a diversity of gases using a theory which complements that for strong and weak acids and bases by Pearson and others (10) and is commensurate with several established gas-surface interactions (11,12). This approach has been formulated (13) to create selective surface coatings. Table 1 demonstrates a selection of hard and soft acids and bases. By monitoring the trends in hard and soft acid and base behavior, first order selections for appropriate modifications of the PS hybrid interface with nanostructured metal/metal oxide coatings to create an improved selectivity for different gases is possible. The development of selective nanostructured coatings that reversibly complex with a gas can be based on the combination of hard Lewis acids with soft Lewis bases and vice versa. The technology which is implemented (13,14) on nanoporous silicon layers positioned on porous silicon micropores facilitates the application of nanostructured metals, metal oxides, and nanoparticle catalytic coatings and provides higher sensitivities. Further, within this framework, novel signal filtering techniques (13,15), operative in a pulsed gas environment, are introduced as a means to reliably eliminate false positive signals. A PS nanostructure coated micropore configuration when subsequently coated with tin oxide (NO$_x$, CO) and gold nanostructures (NH$_3$) provides a greatly increased sensitivity to the indicated gases [16]. Employing these considerations, the sensing of NH$_3$ and PH$_3$ is possible at or below the 100 ppb level.

**TABLE 1.** The selective nanostructured coatings are based on the combination of hard acids and soft bases and vice versa.

<table>
<thead>
<tr>
<th>Hard</th>
<th>Borderline</th>
<th>Soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acids H$^+$, Li$^+$, Na$^+$, K$^+$</td>
<td>Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$</td>
<td>Cu$^+$, Au$^+$, Ag$^+$, Tl$^+$, Hg$^+$</td>
</tr>
<tr>
<td>Be$^{2+}$, Mg$^{2+}$, Ca$^{2+}$</td>
<td>Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$</td>
<td>Pd$^{2+}$, Cd$^{2+}$, Pt$^{2+}$, Hg$^{2+}$</td>
</tr>
<tr>
<td>Cr$^{3+}$, Cr$^{6+}$, Al$^{3+}$</td>
<td>SO$_2$, BBF$_3$</td>
<td>BH$_3$</td>
</tr>
<tr>
<td>SO$_3$, BF$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bases F$<em>{-}$, OH$</em>{-}$, H$_2$O, NH$_3$</td>
<td>NO$_2$, SO$_3^{2-}$, Br</td>
<td>H$<em>2$, R$</em>{-}$, CN$_{-}$, CO, I</td>
</tr>
<tr>
<td>CO$_2^{2-}$, NO$_3^{-}$, O$_2$</td>
<td>N$_2$, N$_2$</td>
<td>SCN$_{-}$, R$_3$P, C$_6$H$_5$</td>
</tr>
<tr>
<td></td>
<td>C$_6$H$_5$N, SCN</td>
<td>R$_2$S</td>
</tr>
</tbody>
</table>

**Sensing of Ammonia and Phosphine**

The introduction of gold to the micro/nanoporous PS framework, through electroless metal treatment, selectively modifies the resistance response to considerably improve the detection of NH$_3$ as shown in Figure 1. In this figure, we compare the current response to
the previously published result (14) with the new results achieved using the described fabrication method. The same sensor is tested under the same conditions with 20 ppm NH₃ before and after electroless gold treatment. The new results show a hundreds of Ω resistance change upon exposure to ammonia and indicate that the gold treatment increases the sensitivity to ammonia by almost three times. The response is also reversible and the sensor resistance goes back to its base resistance at the end of each pulsing run. Thus, the response is found to be reproducible and suggests a physical interaction between sensor and the sensed gas consistent with the acid-base concept. For both tests, 3V is applied to the pore region.

![Image of resistance change upon exposure to ammonia](image-url)

**Figure 1.** Response to 20 ppm NH₃ for both an untreated and a AuₓO coated PS sensor for 600 s pulse periods.

![Image of top view, side view, and electroless AuₓO coating](image-url)

**Figure 2.** Top left figure represents a top view of a sensor, top right figure represents a side view of the sensor which has micropores ∼10 µm in depth. The bottom figure shows the electroless AuₓO coating of the inside of the pores where interactions occur.
The introduction of Au xO nanostructures to the micro/nanoporous framework produces an enhanced sensitivity. SEM images of this coating and pore structure are shown in Figure 2. Nanopore coated micropores provide interaction sites for electroless gold coating, decrease the base resistance of the sensor significantly, resulting in lower heat dissipation and enabling lower power consumption. Recent results obtained for phosphine indicate detection levels much less than 1 ppm.

![Phosphine Detection](image)

**Figure 3.** The PH₃ response of an untreated PS micro/nanoporous surface. The first 300 s corresponds to an N₂ purge for resistance stabilization. PH₃ is pulsed every 600 s following the line purge. R₀ represents the base resistance of the sensor before PH₃ pulsing.

Figures 1 and 2 and the previous studies (14,15) suggest that the proper combination of nanostructure coating techniques on the PS hybrid structure can be used to produce devices of varying sensitivity and selectivity and that a matrix of array responses can be generated to analyze gas mixtures. For example, an array of an SnO₂ and gold clustered oxide nanocoated sensors could be used to sensitively test for the presence and relative concentrations of ammonia and nitric oxide (14) and provides a basis for developing a very sensitive room temperature nitric oxide detector that could be installed in a simple sensor system for asthmatics (14). The outlined nanocoatings are formed using electroless metal solutions (17). There are several other complimentary methods that might be used to produce gas selective nanocoatings on the nano/micropores of PS. These include short-term electron beam deposition, atomic layer depositions and direct nanoparticle diffusion into the PS micropores. An extension to the detection of several additional gases including PH₃ (18), acetone (19), and benzene (20) (in addition to NH₃ (14,22) and HCl (14,22) ) can be made possible using specially designed aluminum oxide (atomic layer deposition or e-beam) or alumino-silicate nanostructured surfaces (18), nickel (electroless) or zirconium oxide based (nanostructured ZrO₂ nanoshells (21) deposited into the micropores of PS) nanostructured surfaces (21), and nitrided titanium dioxide (20) (TiO₂₋ₓNₓ (22,23)) nanostructure coatings. It is possible to expand the list of gases with the development of a more general selective coating technology based on the extrapolation of the concepts of hard and soft acids and bases.
For noise reduction/separation, we have developed a gas pulsing method. Through the introduction of this technique and frequency analysis, the linear low pressure gas response of the PS sensor can be separated from the effects of pressure, temperature, and humidity, and acquired, and filtered on a drifting baseline, further increasing sensitivity. Figure 4 shows a typical pulsing experiment. The baseline for the device increases and plateaus as the adsorption and desorption of ammonia begin to equilibrate, but the signal is not saturated. However, the system might also be affected by low frequency changes in temperature and pressure. By introducing a Fast Fourier Transform (FFT) analysis to the PS gas sensor, the gas response can now be acquired and filtered on a drifting baseline or in the presence of these external noise sources. Since the applied pulse frequency is known, external noise can be eliminated and false positives can be investigated.

Figure 4. 5 ppm ammonia pulsing on a porous silicon sensor. The ammonia is pulsed on and off every 30 s.

An important problem which plagues chemical sensors is the potential contamination of the sensor surface and the elimination of the sensor response over a long period of time. We have managed to treat sensors which have stopped responding for over one year as we rejuvenate their response. The ammonia response of such a sensor to 1,2,3,4,5 ppm of ammonia before and after the rejuvenation process is shown in Figure 5. The recovery of the sensor is clearly indicated.

Figure 5. Response to 1 to 5 ppm NH₃ before and after rejuvenation of an old sensor.
Conclusions

PS sensors has gained considerable interest in the last two decades and, since then, a variety of gas sensor configurations for different types of gases have been proposed. The large surface area and relative ease of modification of its surface enables fast and reproducible detection of organic vapors, H$_2$O, CO$_x$, NO$_x$, NH$_3$, O$_2$, H$_2$, HCl, SO$_2$ and H$_2$S. Recently, PH$_3$ at ppb levels has been detected and a very sensitive ammonia detection has been achieved by improved Au$_x$O nanostructured PS surface modification. A model considering the acid-base character of the interacting molecules and coatings has also been discussed. The results presented demonstrate that PS can be utilized as a promising gas sensor.

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References


