An integrated optical hydrogen sensor on a silicon-on-insulator platform: Effects of palladium film thickness

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A R T I C L E   I N F O

Article history:
Received 18 November 2014
Received in revised form 23 March 2015
Accepted 28 March 2015
Available online 14 April 2015

Keywords:
Sensors
Integrated optics devices
Hydrogen sensor
Optical sensing

A B S T R A C T

In this paper, we present the design and experimental demonstration of a silicon-on-insulator based optical hydrogen sensor. We analyze the response time, hysteresis and sensitivity of our device for various palladium film thicknesses. For a 1 nm thick palladium film the response time is approximately 6 s and the sensor suffers little from hysteresis effect. These attractive features make the sensor highly useful for a wide range of applications.

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1. Introduction

The high price and volatile supply source of oil as well as the desire to move towards greener sources of energy have created a growing interest in the use of alternative fuels, such as hydrogen. The global hydrogen and fuel cell market is poised to be worth $8.5 billion by 2016 [1]. As hydrogen gas is odorless, colorless, tasteless, and can be explosive in volumetric quantities as low as 4% [2], it is vital to have an inexpensive device that can quickly, reliably and safely monitor hydrogen concentrations in case there is a leak. Optical hydrogen sensing offers a number of advantages over competing technologies including compact size, increased safety and immunity from electromagnetic interference. Most optical hydrogen sensors reported to date are based on optical fibers [3–7]. Silicon-on-insulator (SOI) is an excellent platform for implementation of optical sensors, since SOI based optical waveguides are very compact and are easy to mass produce using CMOS fabrication technology. In addition, SOI has the potential to integrate electronics and photonics on the same platform. Many different sensing channels can be integrated on a single SOI chip in order to create an optical nose that would be able to detect multiple environmental variables simultaneously. Despite all the advantages of SOI waveguides for hydrogen sensing, there have been only few reports on SOI-based hydrogen sensor [8–11] and many important questions remain unanswered. One such issue is the effect of Pd thickness on sensor performance. It has been reported for various types of hydrogen sensors that the thickness of palladium (Pd) film has a significant impact on the performance of the sensor including its response time, sensitivity and hysteresis [12]. The aim of the present work is to present a detailed analysis of SOI-based hydrogen sensor with an emphasis on the role of Pd thickness on sensor performance. Such an analysis will enable one to better assess the usefulness of these sensors for practical applications. The paper is organized as follows. In Section 2, we briefly describe our sensor design, fabrication methods and the experimental setup used for sensor characterization. We fabricated a series of sensors with various Pd thicknesses. Test results for these sensors are presented in Section 3. From our experimental results, we observed a number of trends in sensor performance. We discuss these trends, and provide some physical explanation causing these trends in the same section. We conclude the paper with a summary of our observations in Section 4.

2. Materials and methods

2.1. Principle of operation and implementation of sensor

A schematic of the hydrogen sensor is shown in Fig. 1(a). It consists of a rib waveguide partially covered by a thin Pd film. The waveguide mode interacts with the Pd layer as it propagates along the waveguide. When the sensor is exposed to hydrogen, Pd
becomes palladium hydride, and there is an associated change in the complex permittivity of the metal film. The degree of change of Pd film depends on the concentration of hydrogen. Therefore, by measuring the change in transmission, one can estimate the hydrogen concentration. The sensor is fabricated on a SOI substrate, which has a 220-nm thick waveguide layer separated from the silicon substrate by a 3-μm thick silica lower cladding layer. We chose to use single-mode, rib waveguides for our sensor design, since the mode size is larger for these guides compared to silicon nanowire waveguides, and coupling to fiber is more efficient. To ensure that the sensor is compact, the waveguide dimensions were designed to ensure that light transmitted through the sensor strongly interacts with the Pd film, i.e. light should experience large attenuation, while propagating through the sensor. Fig. 1(b) shows the transmission loss calculated by lumerical mode solution for the transverse electric (TE) polarization for various choices of waveguide dimensions when the sensor is coated with a 10-nm thick Pd film. The plot shows that the sensor provides strong interaction with the metal for a wide range of dimensions, and the performance of the sensor is tolerant to fabrication imperfections. In these simulations we assumed that the metal is deposited only on top of the waveguide, and not on the sidewalls. This is a good assumption as the electron beam evaporation process will result in minimal side wall deposition for a thin metal film. In the presence of the metal coating on the sidewalls the transmission loss will be different than those reported in Fig. 1(b), but the device acts as an effective hydrogen sensor in both cases. More details about the sensor design can be found in [13].

The silicon waveguide was fabricated using a combination of electron beam lithography, reactive ion etching and lift-off to produce the final device. The fabrication started with spinning positive electron beam resist ZEP520 on the silicon wafer. The waveguide patterns were defined with a Vistec EBPG5000+ Electron Beam Lithography System in a Class 100 cleanroom. After the pattern was developed, reactive ion etching, using SF₆ and O₂ was used to complete the waveguide fabrication. For the lift-off process, a metalized mask and UV photolithography were used to expose the areas of the waveguides where the Pd was to be deposited. Electron beam evaporation was used to deposit different thicknesses of Pd on the sample. The Pd film was deposited using a BOC Edwards Auto 306 Electron Beam Evaporator equipped with a quartz crystal thickness monitor for real time monitoring of metal thickness. The thickness monitor needs to be properly calibrated to ensure accurate thickness measurement. We prepared a number of samples with various Pd film thickness, and compared the thicknesses predicted by the thickness monitor to those measured by an atomic force microscope. We then used the calibrated thickness monitor to estimate the Pd film thicknesses of the devices we tested. Finally, lift-off was performed to selectively remove the unwanted Pd. Fig. 1(c) shows the final devices.

2.2. Experimental setup

A diagram of the complete setup used for testing the hydrogen sensor is shown in Fig. 2. Light from a Thorlabs S5FC superluminescent diode with 1531.6 nm center wavelength, 60 nm bandwidth, and 21 mW output power was amplified by a JDS Erbium-doped fiber amplifier, and coupled in and out of the sensor using Newport 60° objectives lenses. A fiber polarization controller, polarization beam cube and a half-wave plate were used to control the input polarization. The end fire coupling rig supporting the sample and objective lenses were covered by a polycarbonate box of dimensions 38.5 cm × 18.5 cm × 12.5 cm. Germanium photo detectors were used to monitor the input and output power levels. To minimize the effects of noise, Stanford Research Systems SR830 lock-in amplifiers were used for both input and output signal detection. An optical chopper was placed in the setup after the alignment mirrors to modulate the input light at a frequency of 364 Hz. Although the guide supports both TE and TM modes, the TM mode in high index contrast ridge waveguides are inherently leaky [14]. For this reason, only the TE mode was used in our experiment. We tested the response of our sensor under exposure to various hydrogen concentrations ranging from 0% to 4%. Fig. 2 (left side) shows the setup for controlling the gas composition. Two cylinders containing pure nitrogen and 4% hydrogen (balanced by 96% nitrogen) were connected to a T-junction through two Brooks 5850S mass flow controllers (MFC). A Brooks 0154 control unit was used to control the flow rate of both MFCs. The output of each individual MFC led to a T-junction to mix the gases to achieve the desired hydrogen concentration. The output of the T-junction then led to a union connection on the box. A stainless steel tube then directed the gas flow directly onto the sample, with a sample to tube separation of about 5 mm. A commercial hydrogen sensor from Nova Analytical Systems was used to verify the hydrogen gas concentration in the gas mixture. A custom LabVIEW program was used for both controlling the hydrogen concentration and data acquisition during the experiment.

3. Results and discussions

The most important characteristics of a hydrogen sensor are sensitivity, response time and reproducibility of results under repeated exposure to hydrogen. In the following sections we describe the characterization of the optical hydrogen sensor.

3.1. Temporal response

The temporal detection response experiments were carried out by first exposing a sample to a constant flow of pure nitrogen gas to establish a baseline response. Next, the gas flow was changed from pure nitrogen to 4% hydrogen (with a balance of nitrogen).
Once the sensor response reached a maximum, it was allowed to settle, and then the sensor was flushed with pure nitrogen gas to reestablish the baseline response. We have tested a number of samples with various Pd thicknesses. The waveguide dimensions for all the samples were \( w = 700 \text{ nm}, \ T = 90 \text{ nm}, \ d = 130 \text{ nm}, \ H = 3 \mu \text{m}, \ L = 8 \mu \text{m} \). Fig. 3(a) and (b) shows the response of the sensor to 4% hydrogen concentrations for two different Pd thicknesses (3 and 1 nm). The test results were repeatable over >100 of cycles with no significant change in the response. For both Pd layer thicknesses there was a significant change in transmission in presence of hydrogen, but the transmission was relatively lower for thinner samples. However, the directions of transmission changes were opposite in these two cases. An increase in transmission was observed for the 3-nm think film under hydrogen exposure, while a decrease was observed for the 1-nm thick film under the same condition. To ensure that the response resulted from the presence of hydrogen rather than some other factors, we have also tested the response of an uncoated silicon waveguide under exposure to hydrogen. The change of transmission was negligible in that case, which confirmed that our devices acted as an effective hydrogen sensor.

The change of the response of the sensor for the 1-nm thick Pd film is not unexpected, and consistent with the results reported in previous works [4,15]. A 1 nm film is so thin that it effectively turns the sensor into a nanogap sensor, i.e. instead of a continuous film; we have a series of discrete Pd islands. When the sensor is exposed to hydrogen, the discrete Pd islands expand in volume and connect together to form a continuous film. This is in contrast to the case of Fig. 3(a) where no significant change in surface morphology takes place under exposure to hydrogen. Therefore, it is not unexpected that the sensor behaves differently for the two cases. Although we were not able to verify the island formation for a thin Pd film by conventional SEM, it is possible that the gap geometry is too small to resolve since a relatively low electron beam voltage is required to obtain good contrast for Pd on SOI, which results in lower resolutions. In order to verify island formation, it would be necessary to image the sample with a higher resolution SEM or to cut into the metal with a focused ion beam and image the cross section under SEM. While island formation was not visually verified, we believe there is a strong possibility that island formation for thin Pd film is the reason behind the sensor response change for thinner films.

### 3.2. Hysteresis effect

It is well documented in literature that Pd based hydrogen sensors experience significant hysteresis effect [15,16]. To examine the hysteresis effect of the Pd-hydrogen system on the SOI waveguides and to examine the effect of Pd film thickness on hysteresis, three sensors with different Pd thicknesses were exposed to various hydrogen concentrations. The dimensions for all three waveguides were \( w = 800 \text{ nm}, \ T = 90 \text{ nm}, \ d = 130 \text{ nm}, \ H = 3 \mu \text{m}, \ L = 8 \mu \text{m} \). For each sensor the hydrogen concentration was gradually increased, from 0% to 4% in 0.5% increment, and then decreased again to 0% in
0.5% decrement. After each change in gas concentration, the transmission was allowed to stabilize and measurements were taken before the concentration was changed to the next value. The resultant hysteresis loops are shown in Fig. 4(a) and (b). The change of transmission in response to hydrogen becomes smaller with reduced hydrogen concentration, which degrades the signal-to-noise ratio. For our current experimental setup we estimate that the lower detection limit was 0.5% hydrogen in air.

The most noteworthy feature of the hysteresis loops is their increasing size as the Pd thickness is increased. This can be explained by the clamping effect, which relates the tensile stiffness of a film to its thickness [12]. The thinner the film, the higher the tensile stiffness. For very thin films, this high tensile stiffness limits the amount of volume expansion the film can undergo, which in turn limits the amount of hydrogen that the film can absorb. This clamping effect was discussed in much greater detail by Lee et al. [12]. They measured the resistance of large Pd films after exposure to hydrogen, and determined that thinner films always demonstrate smaller hysteresis loops, and in case of 5-nm thick Pd film, hysteresis can be completely eliminated. We observe the same trend in our experiment, although hysteresis is not completely eliminated. The discrepancy is likely due to the fact that the Pd strips on the waveguides had dimensions on the order of microns, while the Pd layers tested by Lee et al. were deposited onto a 12.5 mm × 12.5 mm piece of silicon, which likely had a much greater tensile stiffness.

3.3. Response time

The response time of a hydrogen sensor is one of the most important metrics to consider in any practical application. It is defined as the time required for the response of the sensor to reach 90% of the change when it is exposed to a steady hydrogen concentration. The United States Department of Energy target for hydrogen safety sensor response time is <1 s for the measurement range 0.1–10% [17]. So far, very few Pd-based hydrogen sensors have been able to demonstrate response times, which even approach that speed, and even fewer over the measurement range of interest [18]. Creating a Pd-based, optical hydrogen sensor that meets those goals and is also robust remains a challenge. To analyze the response time of our device, we have exposed sensors with different Pd thicknesses to various hydrogen concentrations, and recorded the response time. Fig. 5(a) presents the response time for three different Pd thicknesses. The sensor response time significantly decreased with reduction in Pd film thickness, but the response time was always greater than 10 s. The sensor responds much faster for the 1 nm film (Fig. 5(b)). In this case for 4% hydrogen concentration, response time was approximately 6 s.

For all Pd film thicknesses the response time values demonstrated an intermediate peak between hydrogen concentrations of 0.5% and 4%. This peaks shifted increasingly to the right with reduced Pd thickness. We believe the intermediate peaks and the apparent shift in peak location is due to the changing pressure–composition isotherms of the Pd-hydrogen system for thinner films [19]. As the thickness of the Pd film is reduced, there is a reduction in the overall width of the mixed α and β phases (with respect to hydrogen concentration) at a fixed temperature. Combining this with the fact that the hysteresis effect of Pd has been shown to be eliminated for extremely thin films (as a result of completely suppressing the phase transition by reducing the critical temperature of the material) [20], it appears that reducing the film thickness shifts the overall phase diagram curve downward, extending the length of the α-phase, suppressing the phase transition that likely corresponds to the response time peak.
4. Conclusions

In this work, we have presented details of the design, fabrication and characterization of a SOI based hydrogen sensor. The response time is relatively fast (around 6 s for a 1-nm thick Pd film) for hydrogen concentration corresponding to the lower explosive limit (4%). A noticeable hysteresis effect is present due to there being a phase change present as hydrogen concentration increases. However, for a thin Pd film (2 nm or less) the hysteresis effect is considerably reduced. Combination of low hysteresis, short response time and reasonable sensitivity suggest that Pd based sensor is suitable as a safety sensor for small Pd film thickness. The configuration of hydrogen sensor presented in this work is suitable for integration into an optical type node device, which would be able to sense multiple environmental factors (different gases, temperature, humidity, etc.) in a single device.

Acknowledgements

We would like to acknowledge Professor Glenn D. Hibbard of the Department of Materials Science and Engineering for useful advice, and Dr. Pulin Mondal of the Department of Civil Engineering of the University of Toronto for his help in developing the experimental setup. We also thank NSERC for financial support through its CREATE Training Program.

References


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