SILICON-BASED PH SENSOR FOR BIOLOGICAL AND ENVIRONMENTAL APPLICATIONS

BY

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THESIS

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Abstract

In biological and environmental applications, it is desirable to be able to measure hydrogen and hydroxyl ion concentrations (pH levels). Conventionally, the measurement processes take a considerable amount of time involving several calibration steps and handling of fragile electrodes. Here we propose a new, more robust and theoretically reliable way of sensing pH. Following a similar approach to Dr. Qingjun Liu's work on the light-addressable potentiometric sensor (LAPS) from the Zhejiang University in China, we fabricated a silicon pH sensor, with polydimethylsiloxane (PDMS) fluidic channels for solution delivery and testing. Particularly for biological and environmental applications, the range of pH sensing is confined to 6 to 8.

The fabricated device used n-type silicon, so only five acidic solutions between pH 5 and pH 7 were tested. Device test results proved to be somewhat problematic. We were not able to obtain consistent capacitance measurements for a particular pH solution. For some solutions we had extremely large variances in capacitance, yielding “noisy” measurements. However, in retrospect, there are many improvements that could be made to our device and testing procedure in order to obtain more consistent capacitance readings, closer to the theoretical performance. Such changes include modifying the geometry of the electrode which supplies an AC signal for capacitance measurements, and ensuring airtight (PDMS) bonding with the device substrate, guaranteeing seamless solution delivery to the test chamber. It is our hope that future students are able to build upon these results and create a better, more reliable device.
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As for any achievement of my life, I must thank my parents Surya and Lakshmi Gorti for their constant support and parenting from day one of my life. If it were not for all of that, I would not be where I am today.

Two years ago, I began my master's degree here at the University of Illinois, coming from Seattle, Washington, where I had spent most of my life. Despite initially being somewhat of a foreigner, I now realize that I owe thanks to all of the friendly people that I have met here, for easing my transition into a new life. This includes the wonderful and knowledgeable professors who have taught the classes I took, administrative staff of the Electrical and Computer Engineering department, and last but not least the friends I have made in my two years here. Your support will never be forgotten.
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1. Introduction

Hydrogen and hydroxyl ion concentration (pH value) is a measure of the acidity or basicity of an aqueous solution. Typically, the scale of pH is a unitless number between 0 and 14, which indicates the negative decimal logarithm of the hydrogen ion concentration in the solution. A pH value of 7 indicates a neutral solution; solutions with values below 7 are acidic, while those with values above 7 are basic. In most environmental and biological applications, we desire to accurately measure pH in order to characterize various natural processes. Here we propose a novel method of using a semiconductor-based pH sensor which measures ion concentration in a capacitive way.

1.1. Problem Statement

Conventional pH sensors rely on the use of fragile electrodes for voltage measurements. In addition, the process is quite time consuming, requiring pH calibration steps before sample measurement. In recent years, solid state pH sensors have been used for faster measurements. We therefore desire a device which is easy to fabricate, is robust, and measures absolute pH values quickly, without any calibration.

In biological applications, the range of pH values that we are interested in is between 6 and 8. Since this is quite a narrow range, we desire a very high resolution pH sensor – able to detect pH with a tolerance of 0.1. Additionally, pH in biological applications is usually measured for cellular processes. Therefore it is ideal to create a 2-in-1 device in which both cell culturing and growth as well as pH measurement are possible.

1.2. Previous Work

Previous work has been done on a silicon-based surface potential sensor at the Zhejiang University in Hangzhou, China. Dr. Qingjun Liu’s research was on creating an olfactory cell-based biosensor, in which an oxide-semiconductor device (shown in Fig. 1.1) is fabricated for ion concentration measurement (Liu et al. [1]). This device is called a light-addressable potentiometric sensor (LAPS).
The hydrogen and hydroxyl ions released by olfactory neurons on the surface of the device act as the charged gate of a metal-oxide semiconductor capacitor (MOS-C). This gate potential causes a redistribution of charge carriers within the bulk semiconductor (under the oxide). A depletion or accumulation of charge carriers causes a built-in potential to form in the device. Laser illumination from above promotes conduction through the generation of electron-hole pairs. Current is then measured across the device, indicating changes in biological processes.
2. Approach to pH Sensing

Although the LAPS device in [1] is a potentiometric sensor, we chose to implement a similar device, measuring capacitance instead. Please refer to Appendix A for a brief overview on how a metal-oxide-semiconductor capacitor (MOS-C) works. Our device can be modeled as a MOS-C, whose metal gate is replaced with an acidic or basic solution, hence giving the name ion-oxide-semiconductor capacitor (IOSC). The gate voltage is determined by the hydrogen ion concentration in the solution (pH). By applying a small signal voltage across the solution and device, we can measure capacitance across the solution-oxide-silicon interface. Since we are interested in pH values that occur in biological processes, we decide to measure a narrow range of values between 5 and 7.

2.1. Device Fabrication

In [1], a 100 µm thick planar silicon wafer is used as the bulk semiconductor, on top of which 30 nm of SiO$_2$ is grown. On the backside of the wafer, 1µm of aluminum is sputtered. Finally, a 12 mm × 5 mm × 2 mm polydimethylsiloxane (PDMS) chamber was created to culture cells.

Similarly, for the IOSC device we used the following steps to fabricate a slightly modified version. The steps are also illustrated in Fig. 2.1:

1. A 550 µm thick wafer was obtained, which was cleaned using the industry standard RCA clean, which consists of the following the procedure developed in [2]:
   a. A preliminary degrease with acetone -> isopropyl alcohol (IPA) -> de-ionized (DI) water -> IPA -> nitrogen gas (N$_2$) dry
   b. 30 seconds of native oxide etch in a 50:1 DI:HF solution
   c. A 10 minute Standard Clean 1 (SC-1) to remove residual organics and metals. This solution consists of 1800 mL H$_2$O, 360 mL CMOS-grade H$_2$O$_2$, and 180 mL CMOS-grade NH$_4$OH.
   d. 15 seconds of hydrous oxide removal in 50:1 DI:HF
   e. A 10 minute SC-2 to remove remaining contaminants. This solution consists of 1820 mL H$_2$O, 320 mL CMOS-grade H$_2$O$_2$, and 110 mL CMOS-grade HCl.
   f. A final DI rinse and N$_2$ dry
2. On the cleaned wafer, 31 nm of oxide was thermally grown at 1100 °C for 13 minutes using O$_2$ gas flow (dry oxidation). Please refer to Appendix B: Dry Oxidation Curves for dry oxidation curves.
3. Positive photoresist (Shipley 1813) was applied to the top (polished side) of the wafer, while the oxide on the back was left exposed.

4. After a 60-second “hardbake” at 110 °C, a 5-minute buffered oxide etch (BOE) was performed. This ensured that ohmic contact could be made with the bulk on the backside of the wafer.

5. The photoresist was removed using acetone, followed by a standard degrease procedure.

6. 200 nm of aluminum was evaporated on the backside using an electron-beam evaporator at approximately $3 \times 10^{-6}$ Torr.

7. A PDMS mold with fluidic channels (shown in Fig. 2.2) was created using rapid prototyping (stereolithography). PDMS was poured into the mold, removed, and placed on top of the device created in steps 1-6.

![Fabrication steps 1-7 of IOSC device.](image)

Initial experiments were done with a circular solution chamber in the PDMS, simply formed by “punching” a hole through a piece of PDMS. This proved to be problematic since swapping pH solutions during measurement was difficult and left residues in the chamber. To solve this problem,
a fluidic PDMS channel and chamber was created using rapid prototyping. This is shown in Fig. 2.2. The full drawing with dimensions is included in Appendix C. The two inlets allow for mixing two different solutions, which are thoroughly mixed in the winding channel before entering the test chamber. After the capacitance measurements are made, the solution is extracted from the outlet through a syringe.

![Fig. 2.2. PDMS chamber with fluidic channel.](image)

### 2.2. Solution Preparation

For initial experiments, acidic solutions between pH 2 and pH 12 were prepared in steps of pH value 2 using the method described below. These initial solutions were used to test whether the device was fabricated properly, and to test our initial hypothesis of varying capacitance due to pH.

Later, solutions of pH values between 5 and 7 were prepared using standard titration methods. We started with 4 mL of a 9:1 DI:buffer solution, where our buffer was phosphate-buffered silane (PBS). For acidifying the solution, 0.1 M hydrochloric acid (HCl) was used, and to make the solution more basic, 0.1 M potassium hydroxide (KOH) was used. Through trial and error of obtaining each target pH value, we were able to make the following quantities of each pH solution:

- 4335 µL of pH 5.53
- 4185 µL of pH 6.01
- 4125 µL of pH 6.53
- 4160 µL of pH 6.28
- 4066 µL of pH 6.97

pH measurements during titration were done using a conventional glass-electrode pH sensor.
2.3. Device Electrical Model

Please refer to Appendix A for a detailed overview of the metal-oxide-semiconductor capacitor device. From here, we can easily derive an electrical model for the IOSC device. It is safe to assume that our MOS-C-like device will operate in accumulation mode because we are applying a positive bias (positive hydrogen ions) to our gate. Since pH is a measure of hydrogen ion concentration on a logarithmic scale, we can determine the accumulation layer thickness in the semiconductor based on the number of ions (amount of charge) at the surface. The measure of pH is given by Equation 2.1, where \( a_{H^+} \) is the activity of hydrogen ions concentration in mol/L. This value is essentially the concentration of ions multiplied by an activity factor usually between 0 and 1 for aqueous solutions.

\[
pH = -\log_{10}(a_{H^+}) \tag{2.1}
\]

Assuming that \( a_{H^+} = \gamma \times [H^+] \), where \( \gamma \) is the activity factor and \([H^+]\) is the hydrogen ion concentration, we can make an estimate of the accumulation-layer charge that is acquired at the surface of the silicon substrate. Denoting this charge as \( Q_{acc} \), we write \( Q_{acc} = -e \cdot a_{H^+} \), where \( e \) is the fundamental charge constant (1.602 \( \times \) 10\(^{-19} \) Coulombs). Writing this in terms of pH value, yields Equation 2.2:

\[
Q_{acc} = -e \cdot 10^{-pH} \tag{2.2}
\]

Now the oxide potential becomes,

\[
V_{ox} = -\frac{Q_{acc}}{C_{ox}} = \frac{e t_{ox} \cdot 10^{-pH}}{\varepsilon_{ox} A}, \tag{2.3}
\]

where \( \varepsilon_{ox} \) is the permittivity of the oxide, \( A \) is the area of the chamber, where the solution sits, and \( t_{ox} \) is the thickness of the oxide layer. The energy band diagram of the device at equilibrium is shown in Fig. 2.3.
Using Equation A.1 from Appendix A, we are able to estimate the effective gate voltage. First we must know what the flatband voltage is. Silicon’s work function is 4.03 eV [3]. The platinum electrode has a work function of 5.65 eV [4]. The flatband voltage can thus be estimated to be around 1.62 eV. For surface accumulation \( V_g > V_{fb} \), \( \phi_s \) maybe ignored, since it is very small. (The quantity \( V_{fb} \) is explained in Appendix A, but is generally assumed to be zero.) Taking into consideration the work function of the pH solution will make our model very complicated; hence, we will use the term “effective gate voltage” here to denote the voltage of the ionic solution and platinum electrode combined, as seen by the bulk semiconductor, to simplify the model of the device. The effective gate voltage in the accumulation mode of operation can be written as:

\[
V_g = V_{ox} + V_{fb} = \frac{e t_{ox} \cdot 10^{-pH}}{\epsilon A} + 1.62
\]

In accumulation mode, the conduction and valence energy bands bend down near the surface of the semiconductor as shown in Fig. 2.4
In depletion mode \((0 > V_g > V_t)\) the capacitance is affected by the depletion layer width. The depletion region has width \(W_d\). Denoting the depletion charge as \(Q_{dep}\) and the doping density of the semiconductor as \(N_d\), the oxide potential becomes a function of the depletion width, as shown in Equation 2.5. \(\varepsilon_s\) denotes the permittivity of the silicon substrate.

\[
V_{ox} = -\frac{Q_{dep}}{C_{ox}} = \frac{e_t_{ox}N_d W_d}{\varepsilon_{ox} A} = \frac{t_{ox} \sqrt{e N_d 2 \varepsilon_s \phi_s}}{\varepsilon_{ox} A}
\]

\[
\phi_s = \frac{e N_d W_d^2}{2 \varepsilon_s}
\]

The depletion layer width is given by \(W_d = \sqrt{2 \varepsilon_s \phi_s/(e N_d)}\). Combining these equations, we can write the gate voltage as:

\[
V_g = V_{ox} + V_{fb} + \phi_s = \frac{e_t_{ox} N_d W_d}{\varepsilon_{ox} A} + \frac{e N_d W_d^2}{2 \varepsilon_s} + 1.62
\]

The depletion mode energy band diagram of the device is shown in Fig. 2.5. Notice that the band bending is now upward since the gate voltage is positive.
Passing threshold voltage, the device goes into inversion mode of operation. This region of operation is not really of use in the IOSC. In fact, the only region of operation where gate voltage affects pH and vice versa is in accumulation.

2.4. Experimental Setup

Following the fabrication of our device, we performed all of our measurements using the test fixture shown in Fig. 2.6. We used the Agilent 4284A LCR meter, which was capable of measuring capacitance by injecting a small signal AC voltage across its terminals. The LCR meter is connected via a GPIB to USB cable to a PC running Windows Vista, with LabView 8.6 installed. We created a LabView program, otherwise known as a virtual instrument (VI), which was capable of reading capacitance values from the LCR meter, over a certain time period, specified by the user. These measurements would then be exported to an Excel file, containing capacitance versus time data. The user could also specify the DC bias voltage around which the small signal voltage would be supplied. Please refer to Appendix D for details on the LabView application that was created for this application.
Our device was placed on a manually controlled XYZ stage, so that we could keep the position of the device consistent throughout the measurement process. A supporting rod on the test fixture kept the illumination source at a constant height above our device. We used a gooseneck white light source, with three levels of illumination (low, medium, high). In our measurement chamber, through the surrounding PDMS layer, we injected a platinum electrode for pH solution biasing. This was connected to the positive leads of the LCR meter, while the negative leads were connected to the backside aluminum contact of the wafer, using copper tape. Two pieces of long tygon tubing were inserted into the PDMS layer for solution delivery and extraction.
Fig. 2.7. Experimental setup, describing the device in detail and all its connections (see Fig. 2.6 for full experimental apparatus).

For more detail, we provide Fig. 2.7, showing the device and all of its connections. Capacitance is measured between the platinum electrode and the backside aluminum contact of the device. To minimize parasitic capacitance and inductance, wiring was kept as short as possible. Two different PDMS layers were used. First experiments were performed with a PDMS layer which had a 5mm diameter hole punched through it after curing. Fig. 2.8 illustrates this initial PDMS layer prototype. Eventually, a new PDMS layer was engineered with fluidic channels for more efficient solution delivery into the test chamber. That layer was created using the mold shown in Fig. 2.2.

Fig. 2.8. PDMS layer without fluidic channels and just a test chamber.
3. Preliminary Experiments

Before we fabricated the device described in Section 2.1, we performed IV measurements on existing semiconductor devices, namely single-junction silicon solar cells and photodiodes. The purpose of using these devices was to see whether an ionic solution affected carrier transport in the bulk semiconductor in any way. Once the results from these experiments were studied, the device described in Section 2.1 was fabricated. The initial PDMS layer did not contain fluidic channels, and rather was only a slab of PDMS with a hole punched through it. The ionic solutions were deposited into this hole (approximately 5mm in diameter), where the platinum electrode, shown in Fig. 2.6, was also placed so that it was in contact with the solution. Subsequent solution deposition first required the extraction of the existing solution, via syringe. We performed a thorough set of CV curve measurements, to determine the point of maximum sensitivity in our device. This is described in more detail in this chapter.

3.1. Preliminary Solar Cell and Photodiode IV Measurements

Solar cell measurements were conducted using carefully cut pieces of 5 × 5 inch monocrystalline commercial solar cells manufactured by EverBright Solar, Inc. Each of these cells produced 2.5W of power. The photodiodes used were 4 mm-square blue photodiodes ordered from DigiKey (P/N: PDB-C609-2-ND). For both the solar cells and photodiodes, we did not submerge a platinum electrode into the solution, and instead used the given metal contacts on the top and bottom sides of the device. Note that, for these preliminary commercial device measurements, we performed IV measurements rather than CV. Initially we were hoping to see significant differences in IV curves, depending on pH.

The initial set of pH solutions used contained pH values from 2 to 12, rather than the smaller range that we were interested in for biological applications. This also proved to be a useful top-down approach in understanding the sensitivity of our device and in creating our final device which could cater to the smaller desired pH levels.

Solar cell IV measurements were also performed with silicon nanopillar cells which were fabricated in the micro and nanotechnology lab cleanrooms at the University of Illinois. However, for the purpose of determining sensitivity to pH, they did not seem to fare better than the commercial solar cells; for that reason, we disregard that data here.
Fig. 3.1 shows the IV curves for each pH solution deposited on the solar cell. For the commercial solar cells, we noticed that there was a discernible difference between IV curves, based on pH. However, the difference did not necessarily correlate to the pH value. For example, refer to the high light intensity, pH 8 solution and the high light intensity pH 6 solution curves. They nearly follow the same shape, with nearly the same current values. These two curves have the lowest current values within the high light intensity family of curves. From here down, we can see that the rest of the IV curves appear in pairs, corresponding to ion concentration. PH 4 and pH 10 appear next to each other, while pH 2 and pH 12 appear after that. Consider pH 4 and pH 10 – their ionic concentrations are similar, only that they are on opposite sides of the spectrum. PH 4 indicates a high hydrogen concentration, while pH 10 corresponds to a similar level of hydroxyl ions. A possible conclusion that we can derive from this, is that our device is in fact responding to changes in ionic concentrations; however, there is no direct correlation between pH value and reverse bias current of our pn junction.

Fig. 3.1. Solar cell IV curves, with varying levels of illumination and pH solutions. The top set of curves, correspond to low light illumination, while the bottom set is for high light illumination. The key on the right-hand side contains the description for each individual curve, in the format “illumination level – pH value – Solar cell type” (note that No Nanopillars, refers to the commercial EverBright solar cells).
This became one of the first steps in better defining the operational constraints and requirements of our pH sensor. Since it was clear that differentiation between acidic and basic solutions was not quite possible with a semiconductor device, we concluded that our device could only be built for measuring a particular part of the pH spectrum, namely acidic solutions.

Similar measurements were made for the PDB-C609-2-ND photodiode. As an example consider the case of high illumination as shown in Fig. 3.2. There exists a distinction between reverse bias currents based on pH value, but when examined closely, there is once again no clear relationship between pH value and reverse bias current.

![Photodiode Reverse Bias IV Curve High Illumination](image)

**Fig. 3.2.** Photodiode reverse bias IV curves, for pH values between 2 and 12 under high illumination. This data only shows the 3rd quadrant reverse bias current relevant to the operational region of a photodiode/photodetector.
Possible explanations for this behavior in the solar cell and photodiode included the following:

- The ionic solutions were affecting the surface passivation layer of the device, altering electrical properties of the device.
- The passivation layer of the device was too thick for any appreciable effect on IV curves due to pH solution.

It was more than likely that the second explanation was the culprit for our inconsistent data, mainly due to the fact that most commercial semiconductor pn junction devices such as solar cells and photodiodes have very thick passivation layers, on the order of tens of microns. For the amount of charge that is in our ionic solution, this is too thick of a layer to cause any accumulation or depletion of charge carriers in the bulk semiconductor. The IV curves that we recorded were quite close together, and any sort of distinction between them could most possibly be due to noise or inconsistent measurement. After careful thought and verification of this explanation, we decided that in our final device, the insulation layer must be extremely thin – on the order of a few nanometers, the same scale of thickness used by [1].

3.2. Variables
After studying the electrical characteristics of ionic solutions deposited on existing commercial semiconductor devices, we were able to fabricate a device theoretically more optimally suited for pH sensing. This is the device described in Section 2.1. In order to test this device, we needed to first assess the number of variables we were dealing with, carefully noting which ones we could control and which ones we could not. Ignoring most of the trivial variables such as temperature, whose effect on device performance would be negligible, we did a thorough analysis of CV curves, determining the optimal operation point for our device.

3.2.1. Maximum Sensitivity Operation Point
Determining the maximum sensitivity operation point of our device would help us reduce the number of control variables in our experiment and achieve maximum discrepancy between different pH value measurements. In order to do this, we performed a thorough CV analysis of our device at various small signal voltage frequencies and DC biases with a pH 5 solution on top of our device. The CV measurement apparatus was similar to the one illustrated in Fig. 2.6, except that we did not illuminate our device with white light. The tests were done with a makeshift setup in the University of Illinois Undergraduate Integrated Circuit Fabrication Lab (ECE 444), since those LCR
meters were equipped with CV curve tracing. The software used to perform the CV measurements was called Interactive Characterization Software (ICS) designed by Metrics.

CV curves were measured for the pH 5 solution in our device, at frequencies of 20 Hz, 30 Hz, 100 Hz, 1 kHz, 10 kHz, 20 kHz, 36 kHz, 40 kHz, 50 kHz, 60 kHz, 68 kHz, 80 kHz, 85 kHz, 100 kHz, and 1 MHz. (Two trials were performed at 50 kHz to ensure consistency.) The CV sweep was done between –5 and 3 V. Previous CV tracing attempts between –5 and 5 V resulted in the “bubbling” of the ionic solution near the platinum electrode at around 4 V DC bias, causing us to suspect that that voltage was too high for the pH solution, possibly damaging our electrode and our device below.

Fig. 3.3 shows the various CV curves that we obtained, as we manipulated the small signal frequency. Again, there does not seem to be a correlation between frequency and average capacitance. However, through careful analysis of each individual curve, we were able to determine the point of greatest change in capacitance, in other words, the point at which the absolute value of the derivative of the CV curve is greatest.

Fig. 3.3. CV curves at various small signal frequencies. Notice the offset in capacitance as frequency is changed. This offset is not directly correlated with the frequency value.
For all curves, the absolute value of the derivative was maximized around 0.5 V. The frequency range of the curves with the maximum derivative at this point was found to be 50 Hz to 100 Hz. CV curves at 50 and 100 Hz are shown in Fig. 3.4 and Fig. 3.5, respectively. In the 50 Hz curve, a smooth downward sloping curve occurs around DC biases between 0 and 2 V. As mentioned before, we determined the maximum sensitivity point as the point where the downward slope is greatest. That seems to occur in this range.
Notice that at 100 Hz (Fig. 3.5) we see a somewhat “noisy” curve, as indicated by the random fluctuations of the measured capacitance, as the DC bias was swept. Multiple trials yielded similar curves at around 90 to 100 Hz AC signal frequency, confirming that perhaps some external interference, perhaps proximity to a 60 Hz wall outlet signal frequency harmonic, was affecting our measurements. Thus, in order to guarantee “clean” reliable results from the device, we decided not to test it at 100 Hz.

In summary, from the results of the CV curve tracing for our IOSC device at various signal voltage frequencies, we concluded that the optimal sensitivity operation point for our device was at a DC bias of 0.5 V and at 50 Hz signal frequency. The Agilent 4284A LCR meter available in our lab was limited to DC biases of 0, 1.5, and 2 V, due to the lack of a special upgrade capable of doing full CV sweeps. Due to this limitation, we had to set the DC bias to 0 V for testing.

3.2.2. Determination of Control, Independent and Dependent Variables

Now that we had determined two main variables to control, signal frequency and DC bias voltage, it was necessary to analyze the remaining experimental parameters, and determine which ones could be controlled, which ones needed to be measured. The remaining variables that we listed are as follows (ignoring trivial ones, whose effect on device performance would be negligible, such as temperature):

- pH value – this is the main variable we are manipulating.
- Capacitance – the measured parameter of our device.
- Solution volume – the amount of solution that was deposited in the PDMS testing chamber.
- Small signal amplitude – the amplitude of the AC signal used for capacitance measurements. This needs to be kept small in order to avoid clipping, distortion, and excessive biasing of our device.
- Measurement time – the length of time for measuring steady state capacitance value.
- Lighting conditions – whether the test chamber is illuminated or not, and illumination level.
- Device position – relative to the light source; i.e., the height the light source is placed above the device.
- Surface contamination – during successive pH solution tests of our device, we need to keep the surface of our device as clean as possible, especially the test chamber.

It is quite clear that the dependent variable in this case is the capacitance, which is being measured while other parameters are manipulated or kept controlled. The variables we are manipulating
(independent variables) are the solution’s hydrogen ion concentration (pH value) and the lighting conditions. Since we are interested in creating a light addressable sensor, we can choose to test for two different illumination conditions – dark and high illumination.

The rest of the variables listed above are easily controllable. The solution volume would always be constant due to the fixed size of the PDMS test chamber and its input and output channels. Small signal amplitude was set to 0.05 V and measurement time was set to 10 seconds in our LabView program. The device was always placed approximately 2 cm below the light source, and easily controlled with the XYZ stage controls. To deal with surface contamination, we performed a preliminary degrease at the start of each set of tests, and flushed the device with DI water through the fluidic channels after each pH solution was tested. To the best of our ability, we made sure that all of these conditions were kept identical for each set of tests.
4. Experimental Procedure

The experimental procedure that we use for testing the reliability of this device is based on the previous chapter’s results. To reiterate, we determined that the most sensitive operation point is at 50 Hz and at a DC bias of 0 V. We also know that there is higher sensitivity when light is shined in the test chamber. As a result, we devised a procedure where we test each solution from neutral pH to acid continuously using the PDMS channel we had created. We measured capacitance versus time, looking for changes in capacitance as each solution was extracted and the next solution was injected. We tested solutions in order from neutral pH to acidic. The following step-by-step description provides more detail.

1. Perform a preliminary degrease on the substrate without the PDMS layer: acetone -> isopropyl alcohol (IPA) -> de-ionized water (DI water) -> IPA -> nitrogen gas dry (N₂). Perform the same degrease procedure with PDMS layer, disregarding the initial acetone step.
2. Attach the PDMS layer to the silicon substrate ensuring an airtight seal, so that no solution leaks out.
3. Insert the platinum electrode into the test chamber from the sidewalls of the PDMS and the Tygon fluidic tubing at the inlets and outlet. For the experiments described in this thesis, one of the inlets can be completely blocked. If the mixing of solutions is desired, one may choose to insert tubing into both inlets. The rest of this procedure assumes one of the inlets is blocked.
4. Attach a conducting wire on the backside aluminum contact of the device using copper tape.
5. Turn on the LCR meter, and perform an open measurement calibration step for all frequencies (refer to the Agilent 4284A manual for more details on this procedure).
6. Connect the positive lead of the LCR meter to the platinum electrode, and the negative lead to the backside aluminum contact wire.
7. Adjust the XYZ stage knobs so that the device is at the desired height relative to the light source.
8. Ensuring that the GPIB to USB connection is secured between the LCR meter and the PC, open the LabView capacitance measurement application (see Appendix D). Specify the following for each experiment.
   a. Select the GPIB connection in the dropdown menu of the VI (virtual instrument)
   b. Set the DC bias voltage to 0 V
   c. Set the signal voltage amplitude to 0.05 V
d. Set the loop size to 10.

e. Set the iteration length to 1 (this is the length in seconds).

f. Select the desired output folder for the data.

g. Specify the measurement conditions and experiment name – these strings are appended to the file name.

9. In a syringe, fill approximately 100 µL of the desired pH solution, and filling about 1 mL more with air. The extra air is meant to “push” the volume of solution through the tubing into the chamber.

10. Keeping the outlet tubing open, carefully inject the solution into the PDMS channel. Use the extra air accordingly to push the solution through the fluidic channel into the test chamber. Once the chamber is filled, disconnect the syringe from the tubing and keep both inlet and output tubing point upwards, so as to avoid backflow of the solution assisted by gravity.

11. Establish a dark lighting condition. For dark lighting, all ambient light must be eliminated.

12. Run the LabView VI.

13. Repeat step 12 for the desired number of trials for the dark condition.

14. Establish a high illumination condition. For high illumination, set the gooseneck light source to high, with the fiber optic cable craning over the test chamber.

15. Run the LabView VI.

16. Repeat step 15 for the desired number of trials for the high illumination condition.

17. At this point ambient lighting can be restored and the gooseneck lamp source turned off.

18. Use a syringe to extract as much of the solution as possible from the outlet of the chamber.

19. Disconnect this syringe, and use another syringe filled with DI water, to flush out any remaining residues of the test solution through the inlet. Once finished, disconnect the syringe at the inlet.

20. Once more, use a syringe at the outlet to extract DI water from the outlet and disconnect.

Steps 9 through 20 are repeated accordingly for solutions from pH 7 down to pH 5.
5. Results

The results presented in this thesis reflect measurements of two separate sets of experiments. A few initial experiments were carried out, verifying some simple test cases. The first subsection of this chapter describes those experiments in detail. After careful study of the device’s behavior, we formulated the experimental procedure described in the previous chapter. The results of that are presented in the next subsection of this chapter.

5.1. Initial Tests

Despite many attempts to create a robust and reliable device, it became relatively difficult to obtain consistent results from the IOSC device. The first set of measurements was done using the simple PDMS layer with a punched hole for a test chamber. This did not have any fluidic channels. We were able to see a significant difference in the CV measurements. An initial test to see the difference between capacitance of pH 4 and pH 6 solutions was done. PH 6 solution was first deposited in the test chamber, measured for approximately 3 to 4 minutes, then extracted, and replaced with pH 4 solution. The results are shown in Fig. 5.1. There was an appreciable difference in capacitance values.

Another test was done to verify the consistency of these measurements by alternating between pH 6 and pH 4 solutions in a similar manner. Those results are shown in Fig. 5.2. Here there is a maximum of about 30.67 pF of discrepancy between capacitance measurements of the two times pH 6 was deposited, and a minimum difference of 124.1 pF between pH 6 and pH 4 measurements. Two things to note here are that the capacitance values are completely different from those shown in Fig. 5.1 and that there are large variations in capacitance measurements for a single pH solution. This led us to believe that since the test chamber is open at the top, there might be evaporation of the solution, which was increasing capacitance values.
Fig. 5.1. Continual capacitance measurement of a pH 6 to pH 4 solution change.

Fig. 5.2. Continuous capacitance measurement alternating between pH 6 to pH 4 solutions.
5.2. Final Trials

Formulating the final procedure described in the previous chapter, we carried out experiments on our final device which contained the fluidic channels for solution delivery. After many repetitions of the trails, we obtained the best set of two trials for each illumination condition for each solution. In each trial, there are 10 measurement points. All the measurement points of a particular test condition were averaged. These results are presented in Fig. 5.3.

![Final capacitance measurements for the IOSC sensor, for both dark and light illumination conditions.](image)

The entire data set for these experiments is given in Appendix E. There seems to be no distinct correlation between pH and capacitance measurements although from pH 6.97 to pH 6.28 there seemed to be somewhat of an increase in capacitance. However, there was not enough of a distinction of measured values between dark and light illumination conditions. At pH 6.01, there was a definite loss of measurement quality as indicated by the large discrepancy between dark and light measurements. At pH 5.53, it is very likely that the LCR meter was just measuring noise, indicated by the extremely low capacitance values. The variance of the measurements for all pH solutions except 6.97 seemed to be very large, as indicated by Fig. 5.4 and Fig. 5.5. Additionally, it seems that there is a much larger variance of capacitance values under illumination.
Fig. 5.4. Average capacitance values for different solutions under no illumination. Variance bars are included.
One must also note that the overall measurements were greatly error-prone. Eight out of the 172 data points that were taken were improper measurements by the LCR meter. On the LabView VI, this translated to a red data status indicator, yielding either zero capacitance or a maxed-out capacitance value. This led us to believe that capacitance is perhaps too difficult to measure through a wet solution since there is not a proper ohmic contact. The contact resistance of the platinum electrode could also be an issue in providing a proper AC signal through the aqueous solution. The ion concentration in the solution itself could be too low for any significant accumulation in the semiconductor below. For these reasons, we suspect that this way of detecting pH is probably not as reliable as potentiometric sensing as in [1].

There is even some speculation that perhaps there is not a linear relationship between pH and capacitance, as the resulting data shows a parabolic distribution of average capacitance values. In which case, calibration would be required for such a device in field applications.
To verify some of these measurements, we manipulated different experimental parameters such as the AC signal frequency fed through the platinum electrode. Even at higher frequencies, we received very noisy data. Under different lighting conditions, we also received inconsistent data. There did not seem to be a single set of experimental parameters that yielded consistent, unchanging data with time.
6. Conclusions

After spending some time studying the results and evaluating the experience that we had gained thus far, we conclude that there are many ways we could have altered the device and the experimental parameters to ensure more reliability and device durability.

6.1. Device Improvements

One way to alter the device, to produce more consistent results, is to texturize the silicon surface prior to oxidation. Silicon texturizing has been a recently explored method for optoelectronic applications, particularly for solar cells. It is of particular interest in these applications due to its potential for increasing light absorption, and thereby charge collection. The direct implication of this for solar cells is higher electrical conversion efficiencies. Since 2010, many types of nanostructures have been fabricated for solar cell applications including nanodomes [5], nanopillars ([6] and [7]), and nanocones ([6] and [8]). Fig. 6.1 shows the general fabrication procedure implemented by Cui et al. [6] from Stanford University. In this procedure, silicon dioxide nanoparticles are deposited on an epitaxial silicon layer. These nanoparticles act as a mask for a wet etchant which attacks the epitaxial silicon in the gaps between nanoparticles.

![Fig. 6.1. Fabrication procedure for silicon nanopillars and nanocones. [6]](image)

Nanocone fabrication has also been implemented in Professor Gang Liu’s research group at the University of Illinois at Urbana-Champaign as a quick and reliable one-step fabrication procedure, similar to that of [6]. This procedure yields a random distribution of nanocones as seen in Fig. 6.2.
Solar cells fabricated in Prof. Liu’s group have yielded almost 20% conversion efficiency, and more importantly exhibited around 99% absorption in the visible optical frequency range (400 to 700 nm) [8].

With increased light absorption, it can be hypothesized that our device would be more sensitive, when texturized, under illumination.

The nanopillar substrate is created using the following steps:

1. Evaporation of 20 nm of Au
2. Thermal dewetting to form spherical gold nanoparticles on the surface of the silicon (similar to that in [6] shown in Fig. 6.1)
3. 5-minute wet etch to form nanopillars

One other improvement worth exploring is to create an airtight seal of the PDMS to the silicon. Quite often we had to deal with solution leakages due to poor sealing of the PDMS. The device performance could be enhanced by cementing or gluing the PDMS to the substrate below. Then the injected solution would be confined to only the fluidic channel and would not seek alternate exit paths due to pressure differences.

In this thesis, we described a device for measuring acidic solutions using an n-type substrate. However, we did not even consider the effect a p-type substrate would have on carrier transport in our device. Moreover, basic solutions possibly are better detected using an n-type substrate.
Reflecting upon our results, perhaps operating in a different mode (depletion or inversion) would have helped increase discrepancy between capacitance measurements of different solutions.

Lastly, expanding upon what was mentioned in the previous chapter regarding the contact resistance of the platinum electrode, we must consider the option of improving the electrode point of contact with the solution such that the supplied small signal evenly affects the entire volume of aqueous solution. One way to do this is to create a circular plate electrode, which has a better contact with the entire volume of the solution. We can hypothesize that carriers in the semiconductor below would be more uniformly distributed. Contact area mismatch is possibly another reason for poor results. The point of contact of the platinum electrode pales in size with the area of aluminum deposited on the backside.

### 6.2. Improvements to the Experimental Method

Although considerable time was spent on refining our procedure for pH sensing, we must acknowledge that there could be more changes to it that would yield more consistent and useful results. If given more time, we could have explored the actual effect of signal frequency on measured capacitance for more than just one solution and one illumination condition. Given that there are so many variables at work here, there are a vast number of possibilities that could be tried in order to narrow down which experimental parameters work best for pH sensing.

Another thing to consider is that illumination on our device is incoherent. As in [1], perhaps we could have explored the effect of a coherent light source such as a laser on device sensitivity. Expanding upon that, perhaps there is different behavior for different wavelengths of light.

As stated in the previous chapter, we only sought to measure capacitance in our device. Perhaps a more detailed study of CV curves could help us determine what in our experimental method is yielding such “noisy” results. Moreover, IV measurements might yield better discrepancy between solutions of different pH values.

All in all, we have begun experimentation with a very interesting approach to pH sensing that has not been widely explored. We believe that the results described in this thesis are the first of many to come in the engineering of a reliable pH characterization device that would not only speed up many environmental and biological studies, but perhaps even drastically change understanding of biological processes in the medical field.
**Appendix A: MOS Capacitor Overview**

Most of the material in this appendix has been taken from [3]. More information about MOS capacitors can be found there.

The metal-oxide semiconductor capacitor (MOS-C) consists of a moderately doped bulk semiconductor material (in our case, n-type silicon), whose top surface is insulated with an oxide layer (silicon dioxide), on top of which is a metal contact. On the bottom surface of the bulk, is also another metal contact layer. The metal contact on the top is referred to as the gate. All of this is illustrated in the cross-section diagram shown in Fig. A.1.

![Fig. A.1. n-MOS-C cross-sectional diagram.](image)

The MOS-C is a two terminal device, essentially working like a variable capacitor, whose capacitance changes with the gate voltage applied. The charge in the metal gate (the applied voltage at the gate), manipulates the concentration of charge carriers in the semiconductor near the insulator-bulk interface. There are four different modes of operation for the MOS-C device. The band diagram of each of these modes is shown in Fig. A.2.

The trivial case is where there is no gate voltage applied, and thereby no charge on the gate metal. There is no band bending in the semiconductor, and all energy bands remain “flat”. This band diagram is shown in Fig. A.2 (a). There is a difference in energy between the work function in the semiconductor and the work function in the metal. This difference is called the flatband voltage. The gate voltage can always be described as the sum of the flatband voltage, the voltage across the oxide, and the voltage drop across the semiconductor (Equation A.1)
\[ V_g = V_{fb} + V_{ox} + \phi_s \]  \hspace{1cm} (A.1)

For positive gate voltages, larger than the flatband voltage \((V_g > V_{fb})\), we encounter an accumulation of majority charge carriers (electrons) in the semiconductor, which are attracted to the positive charge in the gate. The band diagram is shown in Fig. A.2(b). Here, the capacitance of the device is solely dependent upon the capacitance across the oxide layer, given by Equation A.2, where \(\epsilon_{ox}\) represents the permittivity of the oxide layer, \(A\) is the area of the gate, and \(t_{ox}\) is the thickness of the oxide.

\[ C_{ox} = \frac{\epsilon_{ox}A}{t_{ox}} \]  \hspace{1cm} (A.2)

In accumulation, there is little voltage drop across the semiconductor, so the \(\phi_s\) term in Equation A.1 can be ignored, yielding a gate voltage dependent upon the flatband and oxide voltages only \((V_g = V_{fb} + V_{ox})\).

![Band diagrams](image)

Fig. A.2 Band diagrams of the n-MOS-C in different modes of operation: (a) equilibrium, (b) accumulation, (c) depletion, and (d) inversion.
For gate voltages below the flatband voltage, majority charge carriers (electrons) at the surface get repelled away from the like charges in the gate. As a result, we observe a depletion of carriers at the surface. The band diagram of this behavior is depicted in Fig. A.2 (c). In this region of operation, capacitance becomes a function of applied gate voltage. In depletion, the capacitance of the device is equivalent to the oxide capacitance in series with the depletion layer capacitance in the semiconductor, $C_d$. This is described in Equation A.3, where $C_{ox}$ is given by Equation A.2, $\varepsilon_s$ is the permittivity of the semiconductor, and $W$ is the depletion layer width given by $W_d = \sqrt{(2\varepsilon_s\Phi_a)/(eN_d)}$, where $N_d$ is the doping concentration of the semiconductor.

$$C = \frac{C_{ox}C_d}{C_{ox} + C_d} = \frac{C_{ox}}{1 + \frac{\varepsilon_{ox}W_d}{\varepsilon_s\ell_{ox}}} \quad \text{(A.3)}$$

As the gate voltage goes further below the flatband, the energy bands near the surface of the semiconductor bend further upward. At threshold voltage ($V_g = V_t$), the intrinsic energy level $E_i$ of the semiconductor crosses the Fermi level. Beyond this point, the device is in inversion mode, indicating that the surface now is composed of excess minority carriers (holes) (band diagram is shown in Fig. A.2 (d)). In the case of very strong inversion, assuming that the thickness of the semiconductor layer is large enough, the depletion layer does not increase past a certain point. At that depletion width, which we will denote by $W_{d,max}$, capacitance becomes constant, given by Equation A.4.

$$C = \frac{C_{ox}C_d}{C_{ox} + C_d} = \frac{C_{ox}}{1 + \frac{\varepsilon_{ox}W_{d,max}}{\varepsilon_s\ell_{ox}}} \quad \text{(A.4)}$$

It is often the case that we measure capacitance with a small signal voltage, in which case, the CV curve of the MOS-C device becomes dependent upon the small signal frequency. In inversion, for low frequencies, the contribution of the depletion capacitance is negligible, and can therefore be ignored, making the total capacitance equal to the oxide capacitance. For higher frequencies, total capacitance is more affected by the depletion capacitance, yielding Equation A.4 for total capacitance. The overall CV curves for the MOS-C device are given in Fig. A.3.
Fig. A.3. CV curves detailing the three main modes of operation. The red curve shows a low-frequency CV curve, while the dotted black curve shows high-frequency operation of the device.
Appendix B: Dry Oxidation Curves

The following figure (Fig. B.1) shows the oxide thickness vs. time relationship of dry furnace oxidation (i.e., when only O\textsubscript{2} gas is flowing). In order to grow the 31 nanometers of oxide, we established that a 13-minute furnace oxidation step was necessary. The curves were obtained from [9].

Fig. B.1. Dry oxidation thickness versus time.
Appendix C: PDMS Mold Drawing

This appendix shows the following drawing of the PDMS mold that was created for solution mixing using rapid prototyping. The drawing was created in SolidWorks, which generated the following diagram in Fig. C.1. The 7 mm diameter cylindrical structure shapes the test chamber in which the platinum electrode is inserted after the PDMS is cured. The thinner cylindrical protrusions at the top of the channels define the inlets and outlet of the fluidic channels. After the PDMS is cured, these protrusions shape the PDMS in such a way that a hole can be pierced in the necessary inlets and outlets for Tygon tube insertion.

Fig. C.1. SolidWorks drawing of PDMS fluidic channel.
Appendix D: Continual Capacitance Measurement LabView Virtual Instrument (VI)

In order to perform continual measurements of the IOSC device, we modified a LabView VI example titled “Agilent 428X Series Continual Measurement”, available for download on National Instruments’ Instrument Driver Network page (http://sine.ni.com/apps/utf8/niid_web_display.model_page?p_model_id=264). The modified program’s control interface looked like Fig. D.1. Its block diagram is shown in Fig. D.2. To explain the various controls, we will break down the VI control surface as shown in Fig. D.3.

Fig. D.1. IOSC continual capacitance measurement custom LabView VI control interface.
Fig. D.2. IOSC custom LabView VI block diagram.
Fig. D.3. IOSC VI control panel’s main input groups.

The numbered boxes in Fig. D.3, are explained in more detail:

1. **VISA Resource Name**: Here we select the GPIB interface, so that the VI knows to communicate with the LCR meter through that connection.

2. **Frequency**: The small signal voltage frequency is entered here.

3. **DC Voltage**: The DC bias around which the AC voltage signal is centered is entered here.

4. **Time Measurement Parameters**: “Loop Size” refers to the number of iterations of size “Cycle Time” (in seconds) the measurement will run for. In other words, “Loop Size” defines the number of data points in our measurement, while “Cycle Time” defines the time between each measurement.
5. **File Saving Parameters:** The VI will write all capacitance measurements of a single trial to a CSV file. The user is allowed to specify the illumination conditions in the “Condition” field, an “Experiment Name” which can describe the pH value of the solution, and trial number.

6. **Error Frame:** This frame will print error messages in the case of miscommunication with the LCR meter.

7. **Capacitance Readings:** Here, one will see measured capacitance values and D values (refer to the Agilent 4284 manual), updated in real time. A stop button allows the user to halt data collection at any time. Additionally, there is a data status indicator which is yellow when data is properly received, and red when there is bad data.

8. **Capacitance vs. Time Graph:** In addition to the real-time capacitance readings, capacitance versus time measurements are graphically displayed in this pane.
Appendix E: Final Experiment Results

The complete collection of data on the final experiments is presented in this section in Table E.1. Empty cells indicate that we received data errors for those particular data points (either zero capacitance or a maxed-out measurement). Those data points have been excluded from all analysis.

Table E.1. Complete data set of capacitance measurements

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