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**Abstract.** This manuscript reports on the development of a needle-type sensor for *in situ* on-site measurement of pH. Conventional pH microelectrode sensors are fabricated by pulling glass pipettes and applying ion-selective films at the tip. However, these sensors suffer from low fabrication yields and short sensor lifetime due to disruption or loss of the ion-selective membrane after repeated use. The developed needle-type sensor is fabricated by meniscus etching and takes advantage of the MEMS batch fabrication techniques. The sensor is based on the ion-selective properties of iridium oxide film, which was deposited at the sensor tip by electrodeposition. The sensor exhibited a Nernstian response with sensitivity of  $\sim 62$  mV/pH in the pH 2 to 12 range. The sensor also exhibited a fast 5 s response and a lifetime of  $\sim 2$  months when stored in a pH7 buffer solution, which is substantially longer than that of the conventional pulled-pipette sensors. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: 10.1117/1.3580751]

Subject terms: MEMS; pH sensor; electrochemical sensor; electrodeposition; microelectrodes.

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## 1 Introduction

Needle-type sensors offer the ability of penetrating samples for measurements. This is in contrast to the conventional lab-on-a-chip or FET-based sensors which require sample collection. Without sampling, measurements could be performed *in situ* or on-site, and analyte concentration microprofiles can be determined by controlling sample penetration depth. The small dimensions of the sensor are also more practical for probing live bacterial films (biofilms)<sup>1</sup> or cellular chemistry.<sup>2</sup>

In the last two decades, needle-type sensors (microelectrodes) with tip diameters of  $< 10$   $\mu\text{m}$  have been developed.<sup>3</sup> These sensors can be fabricated in a number of ways. Most commonly, microelectrodes are fabricated by pulling a glass pipette, inserting a metal wire such as Pt or Au, and then filling with a low-melting-point alloy. Fabrication of ion-selective electrodes requires the use of ion-selective liquid membranes that must be filled at the pipette tips; a polymer matrix is typically used to trap the membrane in place. Although these fabrication methods are well-established, a number of inherent disadvantages still exist, such as low success rate, poor reproducibility, fragility, loss of ion-selective

membrane after repeated use, and difficulty in making a multianalyte sensor.<sup>1,3</sup>

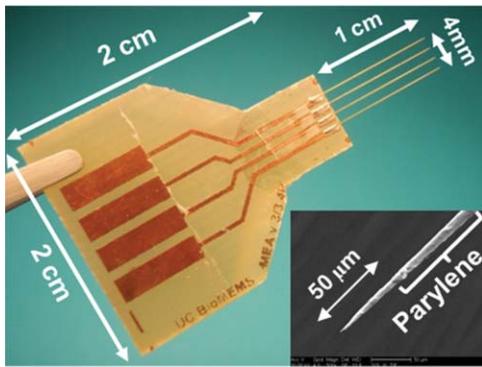
Microelectromechanical system (MEMS) technologies can offer many advantages to fabrication and integration of sensors, including reduced sensor complexity, increased reproducibility (and yield) of the fabrication process, and reduced costs due to batch fabrication. We recently applied MEMS technologies to the development of microelectrode arrays (MEAs) for measurement of the oxidation-reduction potential (ORP)<sup>4,5</sup> and dissolved oxygen (DO).<sup>6,7</sup> ORP is a measure of the solution potential and thus ORP MEA sensors are non-specific and measure the oxidized and reduced forms of all chemical species in the solution. DO MEA sensors are ion-selective and exhibit sensitivity to oxygen due to the recessed structure of the gold cathode. The resulting sensors have tips on the order of 1  $\mu\text{m}$ , and are much smaller than the conventional sensors.

Herein, we report on the use of MEMS technologies to demonstrate a needle-type pH sensor. Sensing of extracellular pH can be used to detect perturbation in bacterial or cellular metabolism. The sensor is based on the ion-selective properties of iridium oxide (IrOx). The main advantages of IrOx in comparison with other pH sensitive films include a wider pH response range, high sensitivity, and low redox pair interference.<sup>8</sup> The half-cell potential generated at the interface between the electrodeposited IrOx and the electrolyte depends on  $\text{H}^+$  concentration, and follows the Nernst equation. The previously reported ORP and DO microelectrode array sensors used a gold electrode surface for measurement. Introduction of a solid ion-selective film is a critical step toward realizing a multianalyte MEMS needle-type sensor array.

## 2 Experimental Methods

A microelectrode sensor array was fabricated from glass wafers as reported previously.<sup>4-6</sup> A representative photograph is shown in Fig. 1. Briefly, sensors were fabricated from 175  $\mu\text{m}$  thick,  $25 \times 75$   $\text{mm}^2$  glass wafers. Each glass wafer was diced and meniscus etching in a buffered solution of hydrofluoric acid (HF) was used to sharpen microelectrode shafts [Fig. 2(a)]. In this approach, glass probes are immersed in the etchant solution with an immiscible organic layer (oil) on top. The meniscus height at the etchant-probe interface is dependent upon the contact angle as well as size and spacing of the immersed probes. As time progresses, the probe size decreases due to etching, causing the meniscus to fall slowly and resulting in a tapered tip. This method is self-terminating, eliminating the need for timing the etch process. As we discussed previously,<sup>9</sup> the tip length and angle can be controlled by modifying process parameters such as composition of the etchant or the organic layer. The etched electrode array was coated with Au/Ti layer (200 nm/20 nm) by evaporation.

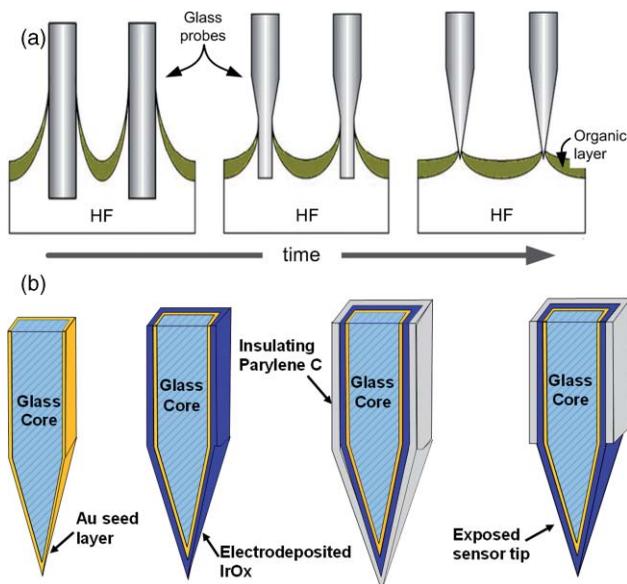
We used electrodeposition to form an iridium oxide layer for the pH sensor tip [Fig. 2(b)]. This was accomplished using a Gamry Reference 600 potentiostat in galvanostatic mode. Prior to electrodeposition, Au tips were cleaned in piranha ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  7:3 v/v) for 10 min. Two gold plates (1-mm thick, 3 cm  $\times$  5 cm each) were used as dual cathodes. The electrolyte solution was prepared by mixing iridium tetrachloride, hydrogen peroxide, oxalic acid, and anhydrous



**Fig. 1** Photograph of a packaged needle-type sensor array. All four needles of the array are IrOx pH sensors. An inset illustrates a scanning electron microscope image of a sensor tip, indicating parylene C insulation and the exposed 50- $\mu$ m long tip area.

potassium carbonate in deionized (DI) water.<sup>10</sup> Specifically, 150 mg of iridium tetrachloride was dissolved in 100 ml of DI water and stirred for 20 min. Then, 1 ml of 30% hydrogen peroxide was added and stirred for 15 min. 0.5 g of oxalic acid was added and stirred for 5 min. Solution pH was adjusted to 10.5 using anhydrous potassium carbonate. The color of the fresh solution was light yellow, which changed to light violet after stabilization at 90 °C for 10 min.<sup>10</sup> The electrolyte was then chilled in stirred cold water. The electrolyte could be re-used for more than 50 depositions within a 2 month period if stored in an amber bottle in a refrigerator at 4 °C. Dark blue iridium oxide films were obtained with the current density of 1 mA/cm<sup>2</sup> for 8 min electroplating, yielding a thickness of  $\sim$ 250 nm.

We used enamel to affix each array on printed circuit board (PCB) carriers and conductive silver epoxy to form electrical



**Fig. 2** (a) Needle-type sensor tip fabrication by self-terminating meniscus etching. (b) Fabrication of IrOx sensing tip. A thermally evaporated Au seed is first coated by IrOx using electrodeposition. Parylene C is then thermally deposited for insulation, and the tip area is exposed for sensing by oxygen plasma.

connections between the sensor needles and copper traces. A 1- $\mu$ m thick layer of Parylene C was deposited over the entire microelectrode array surface for insulation; 3M tape was used to protect electrical contact pads on the PCB during the deposition process. The tips of individual electrodes were exposed by oxygen plasma (20 sccm, 50 W) for 5 s to generate sensing areas. We used photoresist (Shipley 1818) to protect microelectrode shafts during this oxygen ashing process and mounted each array vertically (tips up) to ensure selective parylene removal at the tips.

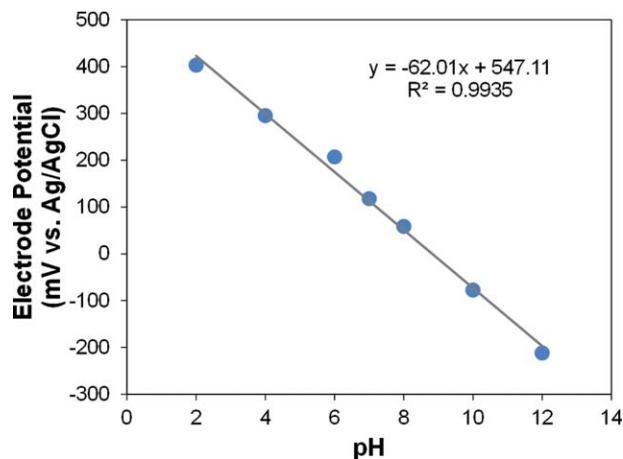
The pH sensor was calibrated using standard buffer solutions of pH 2 to 12 (Fisher Scientific), with a multimeter (Model 225, Denver Instruments) used for potential measurements. A LABVIEW (v.7) program was used to acquire data from the multimeter via RS232 port, and record potential data as a function of time. An external commercial Ag/AgCl microelectrode, (MI-401, Microelectrodes, Inc.) was used as a reference.

### 3 Results and Discussion

In electrochemical sensors, the working electrode surface plays a critical role as it influences the ability of the analyte to interact with the surface and therefore be detected. Thus, the working electrode surface roughness (or rather surface smoothness) is important and was investigated. The AFM analysis indicated surface roughness of  $\epsilon_{RMS} \sim 295 \pm 49$  nm. We compared the controlled-current (1 mA/cm<sup>2</sup>) and controlled-potential (0.65 V) deposition conditions, and found the controlled-current approach to be superior. The current density increased constantly during the controlled-potential deposition, which caused difficulties in controlling electrodeposited film thickness by process time. Ultimately, the controlled-potential method yielded films with higher surface roughness, which is not desirable as the needle-type sensors are intended for penetrating biological samples (e.g., biofilms, tissues) for measurements and surface roughness leads to sample disruption as well as difficulties during withdrawal. An electrodeposition rate of  $\sim$ 20 nm/min was measured for the controlled-current IrOx electrodeposition, which offered excellent control of the deposited film thickness.

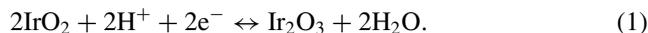
The fabrication yield of the needle-type sensor was improved through the use of MEMS batch fabrication methods and optimization of the selective layer electrodeposition. In the batch fabrication approach, multiple microelectrode arrays were fabricated from a single glass wafer by maintaining wafer integrity until the PCB packaging step. The approach yielded 12 electrically isolated arrays containing 48 microelectrode sensors from each glass wafer. To further increase fabrication yield, the entire exposed sensor tip was coated with IrOx. As we previously reported in our work with electrodeposited phosphate sensors,<sup>11</sup> electroplating at the probe tip is challenging and has low yield due to the small size of the exposed Au film ( $<4 \mu\text{m}^2$  area) which requires a small current (in the 1 pA range) at the limit of the potentiostat capabilities. Controlling such small currents is further complicated by noise and interference, and applying overpotential on the seed layer leads to stripping.

The needle-type pH microelectrode sensor exhibited a linear repose in the pH 2 to 12 range. A representative calibration curve with respect to an external Ag/AgCl reference



**Fig. 3** A typical calibration curve of the IrOx needle-type pH sensor in the pH range of 2 to 12 at room temperature.

electrode is shown in Fig. 3. The sensor exhibited a Nernstian response with sensitivity of  $\sim 62$  mV/pH. This value agrees with results reported in literature for the conventional microelectrode sensor based on an ion selective membrane<sup>11</sup> and the IrOx macroelectrodes.<sup>8,10</sup> A Nernstian response of an anhydrous IrOx film to pH change is described by the following redox reaction;<sup>8,10</sup>



Sensitivity of our sensor remained practically constant during  $\sim 2$  months of storage and repeated use. It is important to note that storage in pH 7 buffer solution was critical to a long sensor lifetime, as it contributed to maintenance of the IrOx layer thorough oxidation. Dry storage of sensors led to a noticeable, up to 25%, sensitivity degradation, monthst likely due to gradual degradation of the IrOx layer and inability to replenish between measurements. These results are a substantial improvement over the conventional microelectrodes based on the ion-selective liquid-membrane, which only last 1 to 3 days due to evaporation of the liquid membrane or disruption during repeated measurements.<sup>12</sup>

Fast response times are critical in biological experiments. Our sensor required approximately 5 s to reach 90% equilibrium value. This is consistent with reports in literature for conventional microelectrodes<sup>12</sup> and IrOx macroelectrodes.<sup>8,10</sup> The typical response time doubled after 1 month of storage and repeated use.

While IrOx can be deposited by evaporation, electrodeposition offers a number of advantages in this work. In addition to simplicity, one of the unique advantages is the ability to selectively coat needle sensors. Since current application is necessary for electrodeposition, application of current to specific pads of a packaged sensor results in selective deposition

of the IrOx film. Thus, this approach offers the ability to selectively deposit metallic films at the tips of specific needle sensors, paving the way to integration of the pH sensor with the previously described needle-type ORP<sup>4,5</sup> and DO<sup>6,7</sup> sensors. Taking this approach further, different metallic films may be deposited at the tips of different needle sensors, permitting future integration of the pH sensor with the recently described phosphate sensor based on the cobalt oxide sensing layer.

#### 4 Conclusions

We have successfully demonstrated an improved needle-type pH sensor. It exhibits performance similar to that of a conventional microelectrode sensor, yet is much monthre robust and offers higher fabrication yields. The sensor is now suitable for intergradations with other previously described sensors, namely ORP and DO. It will be tested with biofilms in the near future.

#### Acknowledgments

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