Miniaturized Planar RTIL-based Eletrochemical Gas Sensor for Real-Time Point-of-Exposure Monitoring

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***Abstract*—The growing impact of airborne pollutants and explosive gases on human health and occupational safety has escalated the demand for sensors to monitor hazardous gases. Existing gas sensors lack the miniaturization and real-time measurement capability necessary to quantify point-of-care exposure to gaseous hazards. To overcome these challenges and enable cost-effective monitoring of personal exposure in local environments, this paper presents a robust microfabricated planar electrochemical gas sensor featuring room temperature ionic liquid (RTIL) as the electrolyte. Together with carefully selected electrochemical methods, the miniaturized gas sensor is capable of measuring multiple gases important to human health and safety. Compared to its larger predecessor, our manually-assembled Clark-cell sensor, this microsensor provides better sensitivity, linearity and repeatability, as validated for oxygen and methane monitoring. The microfabricated planar RTIL electrochemical gas sensor is well suited for personal point-of-exposure monitoring of hazardous gases in a real world environment.**

Keywords—Microsensor, point-of-care, planar platinum electrode, electrochemical gas sensor, RTIL

I. INTRODUCTION

The principle environmental pollutants identified by the EPA's National Ambient Air Quality Standards include NO_2 (nitrogen dioxide), CO (carbon monoxide), O_3 (ozone) and SO_2 (sulfur dioxide) [1], and exposure to such airborne toxins are a leading cause of global illness and mortality [2]. Furthermore, flammable and explosive gases including O2 (Oxygen), H_2 (Hydrogen) and CH4 (Methane) need to be observed regularly for occupational safety. Although a variety of gas sensors have been developed to monitor air pollutants and dangerous gases [3, 4], most existing tools are, unfortunately, incapable of accurately measuring acute exposures that vary with an individual's relative location. An affordable and wearable-sized gas sensor that is capable of real-time point-of-exposure data collection could provide immediate alerts of gaseous hazards to vulnerable individuals. Furthermore, such a sensor could be widely deployed, for example in mobile phones, to provide researchers with vital location- and time-tagged exposure data to develop gaseous hazard health impact models.

Gas sensor technologies with potential for miniaturization into a point-of-care platform include metal oxide semiconductor, piezoelectric, surface acoustic wave and electrochemical. Among these technologies, electrochemical sensing offers a combination of features and performance that is very promising for acute gas monitoring, including low cost, low power consumption, high sensitivity and high selectivity [5]. Furthermore, the instrumentation for electrochemical sensors can be readily formed in CMOS chips [6] allowing the entire sensor system to be realized in a miniaturized format. To overcome the limitations in electrochemical sensors due to solid or liquid electrolytes, multi-gas sensors have been demonstrated using room temperature ionic liquid (RTIL) electrolytes [7-10]. The low vapor pressure, electrochemical and thermal stability and high ionic conductivity of RTILs provide outstanding properties for electrochemical gas sensors with long operation lifetimes. However, existing RTIL-based electrochemical sensors suffer from large physical dimensions and/or long measurement time and/or variability due to the sensor fabrication process that limit their use in point-of-exposure monitoring of gaseous hazards.

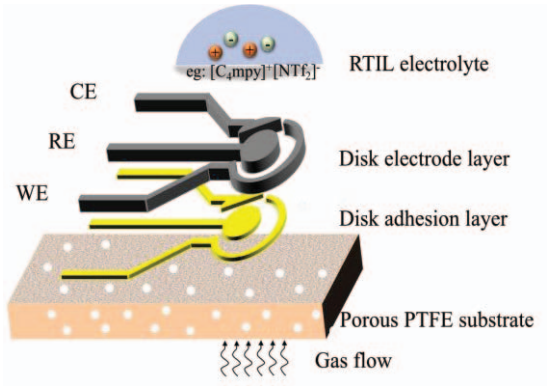

Figure 1. Functional structure of the microfabricated planar RTIL electrochemical (MPRE) gas sensor.

To overcome the limitations of existing gas sensors, this paper introduces a new microfabricated planar RTIL electrochemical (MPRE) gas sensor suitable for point-of-exposure measurement of multiple gases. Evolving from our prior work on a miniaturized gold planar electrode gas sensor [11], the MPRE sensor shown in Figure 1 utilizes a modified fabrication process to improve performance and reliability. Measurement of oxygen and methane are presented to demonstrate high sensitivity, linearity and repeatability.

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II. MPRE Gas Sensor Structure

For gas sensing, electrochemical reactions occur at the so-called "three-phase" interface, where electrode, electrolyte, and target gas are physically connected. In traditional sensor structures [12, 13], RTIL is coated atop a set of electrodes supported on a solid substrate, and gas must diffuse through the RTIL electrolyte to reach the reactive three-phase interface. Because of the high viscosity of RTIL, this traditional structure exhibits a very long response time that limits effectiveness for real-time measurement applications. To improve response time, we previously reported a macro-scale Clark cell that was manually assembled by stacking platinum mesh (working electrode), filter paper (insulator) and platinum wires (counter and reference electrodes) on top of porous polytetrafluoroethylene (PTFE) [10]. The porous PTFE substrate allowed gas to quickly reach to the three-phase interface without diffusing through the RTIL for substantial improvement in response time. However, the manual assembly process limited miniaturization and generated an undesirable performance variation between devices.

To maintain rapid response time while miniaturizing the sensor and eliminating manual assembly variations, our group previously introduced a sensor that formed planar gold electrodes on a porous PTFE substrate using an accurately controlled microfabrication process [11]. The MPRE gas sensor presented in this paper uses the same structure with a new fabrication process that improves reliability and performance. As shown in Figure 1, the MPRE consists of a porous PTFE substrate on which a set of planar electrodes is microfabricated prior to coating the device with RTIL electrolyte. The disk-shaped electrodes are precisely and repeatably patterned using photolithography and are reliably attached the rough porous PTFE surface using a metal adhesion layer. Environmental gases rapidly reach the three-phase electrochemical interface through the porous PTFE substrate.

III. Sensor Fabrication and Packaging

Many traditional microfabrication processes are difficult to perform on porous PTFE substrates due to the flexibility of this material and roughness and porosity of its surface. Based on our prior work [11], PTFE can be affixed to a glass holder to resolve the flexible substrate challenge, and AZ4620 photoresist can be used to form thick layers (~10µm) that permit thin-film metals to be patterned using lift-off on the rough and porous PTFE surface. However, this prior process utilized thermal evaporation for thin-film metal deposition, which introduces high energy metal atoms that can raise the temperature of the PTFE surface higher than 300°C. Above 115°C, PTFE can undergo vitrification, molecular transformation to glass, that introduce stress to the substrate surface that promotes undesired peeling of thin-film metals. Furthermore, it can affect PTFE pour size on the surface that may hinder gas flow through the substrate.

To improve the shortfalls of our prior process, magnetron sputtering was chosen for thin-film metal deposition rather than thermal evaporation. Sputtering releases metal atoms through momentum exchange due to collisions rather than heating and results in less heating of the PTFE surface during deposition. Additionally, the electrode metal was changed to platinum in this design for different electrochemical properties, and a titanium adhesion layer was included to further improve reliability of metal attachment to the rough PTFE substrate. Figure 2 describes the final microfabrication process used to create the MPRE gas sensor. First, a glass slide was cleaned in oxygen plasma and PTFE with 4µm average pour size (POREX PM23J) was affixed by double-sided tape. Then a 10µm layer of AZ4620 photoresist was spin-coated at 2100 RPM on the PTFE surface, and the desired electrode areas were exposed through a photomask. The glass slide was removed and the thick photoresist was developed. Then, 50Å titanium followed by 3000Å platinum was deposited via sputtering. This metal thickness was experimentally determined to form continuous traces on the porous PTFE surface. The planar thin-film metals were then patterned via lift-off of photoresist in acetone overnight followed by ultrasonic vibration for 5 minutes.

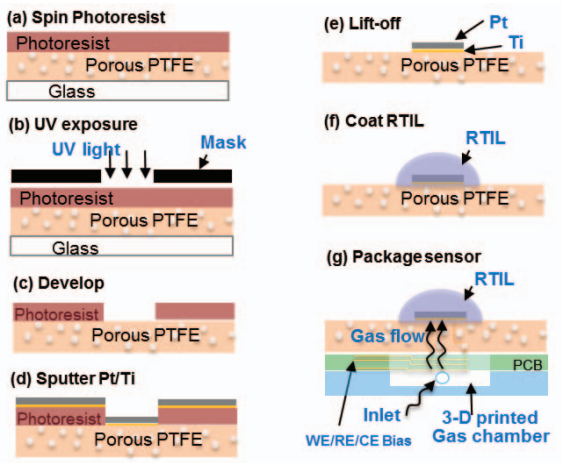

Figure 2. MPRE gas sensor fabrication and packaging process.

Following electrode patterning, an RTIL film was deposited on the surface via pipette to cover the electrode sensing area. The RTIL chemical composition can be tailored to different gas targets. For the oxygen and methane sensing in this paper, 1-butyl-1-methylpyrrolidinium bis-(trifluoromethylsulfonyl)-imide ($[C_4mpy][NTf_2]$) (IOLITEC. Inc.) was used as the RTIL electrolyte.

To complete the MPRE gas sensor, the electrode on porous PTFE device was attached to a custom PCB board and a 3D printed gas chamber, as shown in Figure 2 (g). Gas sensor electrodes were connected to PCB traces using conductive silver epoxy for connection to external instrumentation. A hole was drilled through the PCB beneath the active sensing area, allowing gas to enter the device through the attached low-volume gas chamber.

IV. Results and Analysis

A. Electrode Inspection

Figure 3(a) shows a photograph of two ~7mm MPRE gas sensors prior to RTIL deposition. Figure 3(b) shows a close-up SEM image of platinum electrode topography, and Figure 3(c) provides a side view of a rough spot in the electrode using focused ion beam (FIB). The SEM and FIB images highlight that thin-film sputtering resulted in a rough but

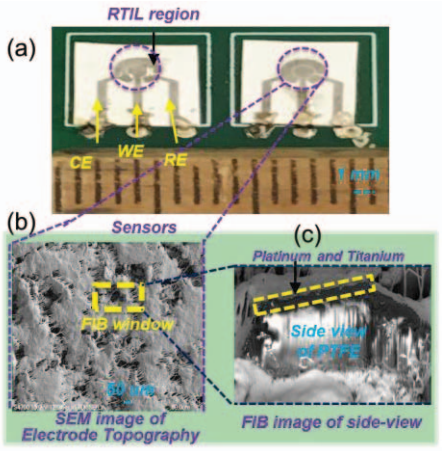

Figure 3. MPRE gas sensor: (a) two disk-shaped electrodes before RTIL coating; (b) SEM image of electrode surface topography; (c) Focused ion beam side view image of the electrode surface.

continuous electrode that is bound well to the porous PTFE surface.

B. Electrochemical Test Setup

Prior to electrochemical testing, the packaged MPRE sensor was placed in a desiccator filled with calcium carbonate to control humility. A CHI 760 (CH Instrument, USA) was utilized for all electrochemical tests. A Gas Blender 103 (MCQ Instrument, Italy) was used for gas mixing and flow control.

C. Oxygen Sensing

The MPRE sensor was first tested for oxygen measurement in N_2 background using constant potential amperometry at -1.2V. The results in Figure 4(a) show that the MPRE sensor exhibits good sensitivity ($0.77\mu A/\%O_2$) and a linear response to oxygen from 0% to 21%. To compare the performance of the MPRE sensor with the manually assembled Clark cell sensor, an additional test was performed for oxygen measurement using double potential amperometry at -1.2V and 0.2V. The Clark cell active sensing area was experimentally determined to be about 100-times larger than the MPRE sensor. Results in Figure 4(b) and the calibration curve in Figure 4(c) show that the MPRE sensor has a significantly higher sensitivity per unit area. To compare repeatability, measurements at each oxygen concentration were performed five times, and results are shown as error bars in Figure 4(c). Calculation of the relative standard deviation shows the MPRE sensor improves repeatability by more than a factor of 8.

D. Oxygen-Methane Coupling Test

A methane-oxygen electrochemical reaction coupling previously developed by our team [10] was utilized to measure the concentration of methane gas using the MPRE sensor. Double potential amperometry at 0.9V and -1.2V was employed for methane oxidation and oxygen reduction, respectively. Figure 5(a) shows the results for methane concentrations from 0% to 6%, which is a typical range of interest for occupational safety applications. The calibration curve in Figure 5(b) demonstrates a methane sensitivity of over $0.3\mu A/cm^2$ was achieved with very good linearity (R^2=0.9991) over the tested range.

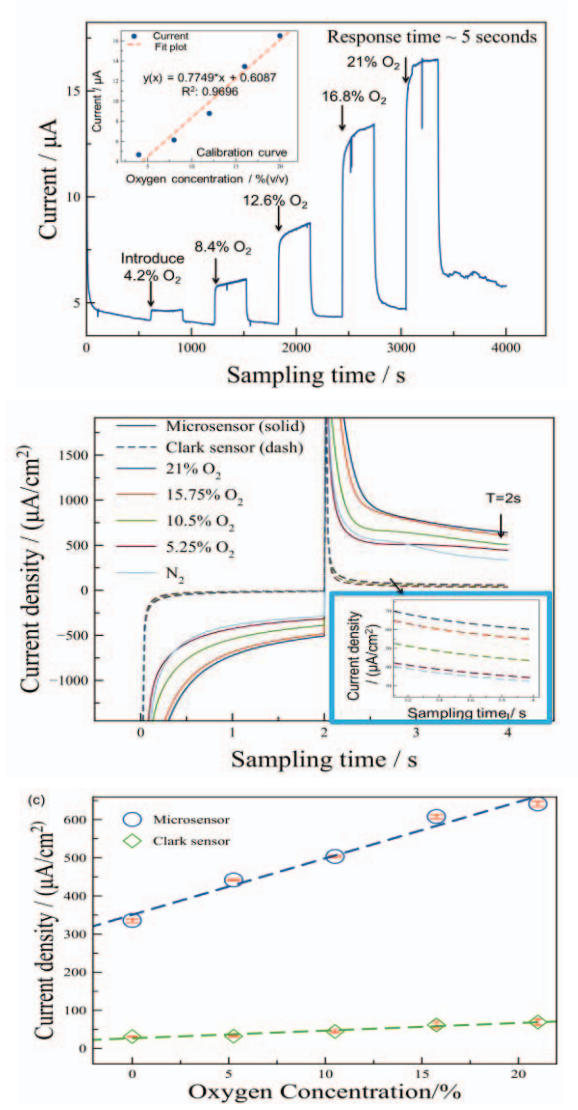

Figure 4. Oxygen sensing results collcected from the MPRE gas sensor: (a) oxygen ameperometric results for different oxygen concentration; (b) comparison between manually assembled Clark Cells and MPRE gas sensor under double potential amperometry method; (c) comparision using calibriation curves.

E. Multi-gas Sensing Results

RTIL-based electrochemical sensors have been shown to exhibit an amperometric response to many additional gaseous hazards important to human health and safety. Figure 6 shows responses collected by our group of RTIL-based electrochemical sensors for CO, SO_2, O_2 and H_2 [14]. Responses to individual gases were obtained using constant potential amperometry at different bias voltages for each gas. The multi-gas sensing capability of RTIL-based electrochemical sensors, combined with the MPRE results reported here, enable future development of a sensor array that can simultaneously measure the concentration of multiple gases in mix-gas pollutant environment. Selectivity can be achieved by judicious choice of electrode materials, RTIL chemical composition and electrochemical method (particularly bias voltage). Thus, the MPRE gas sensor represents an initial step toward a miniaturized, inexpensive, rapid-response, low power, multi-gas sensing array for point-of-exposure monitoring of gaseous hazards.

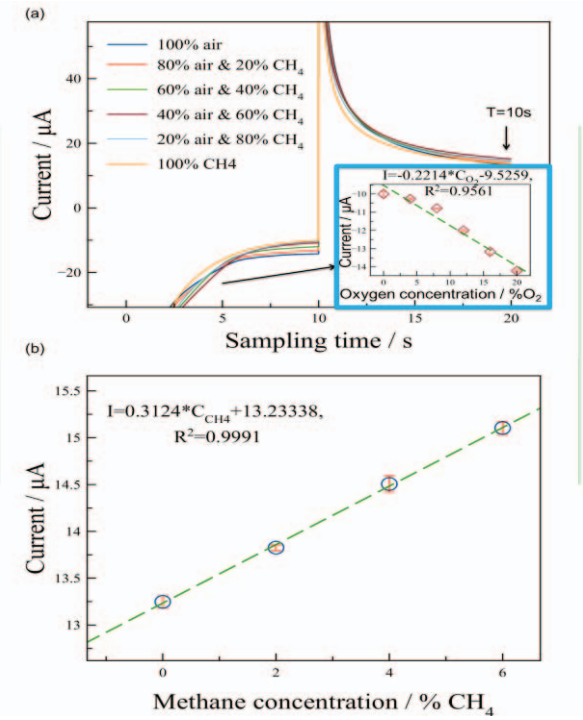

Figure 5. Methane amperomenty test results: (a) methane-oxygen-coupling sensing resuts with different methane concentration; (b) calibration curve of amperometry current vs. methane concentration. The calibration curve of oxygen reduction is shown in the inset of (a).

V. Conclusion

This paper introduced a microfabricated planar RTIL electrochemical gas sensor suitable for point-of-exposure measurement of multiple gases. A detailed fabrication process for the microsensor with improved reliability was described. Test results show the gas sensor has good sensitivity, linearity and repeatability for oxygen measurement. Oxygen sensing performance was also shown to be significantly better than a manually assembled macro-scale Clark cell sensor with a similar structure. Additionally, methane concentration sensing was demonstrated with 0.3µA/cm^2 sensitivity and 0.9991 R^2 linearity value in the range of 0%-6% methane using a methane-oxygen electrochemical coupling method. Combining the miniaturization and performance of the new gas sensor reported here with the multi-gas sensing capability of RTIL-based electrochemical sensors enables a new generation of inexpensive, real-time, low power, gas sensor arrays for point-of-exposure monitoring of gaseous hazards.

Acknowledgment

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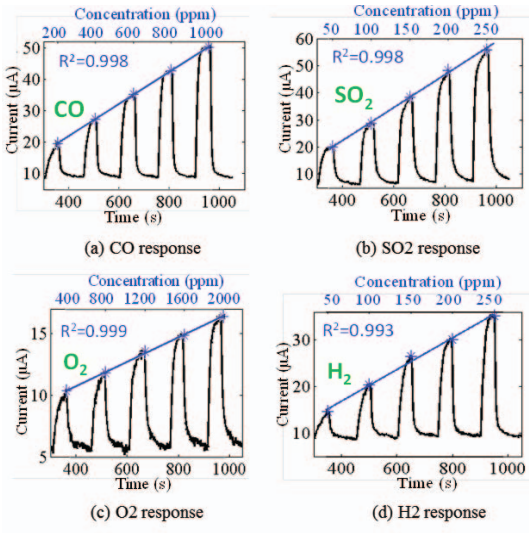

Figure. 6. RTIL sensor responses for air quality monitoring [14]. In the transient response of each gas, the five peaks represent five different concentrations. The valleys between peaks represent the sensor response when the concentrations were set at zero. The asterisks represent the stable sensor output currents at nonzero gas concentrations. The straight lines represent best-fitting lines.

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