

Fabrication of a Miniaturized Room Temperature Ionic Liquid Gas Sensor for Human Health and Safety Monitoring

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Abstract— The growing potential impact of airborne pollutants on human health and safety has escalated the demand for sensors to monitor hazardous gases. Room temperature ionic liquid (RTIL) gas sensors utilizing electrochemical instrumentation demonstrate promising sensitivity, selectivity, and miniaturization capabilities. This paper introduces a microfabrication process that enables miniaturized, rapid response, gas sensors to be realized using RTIL interfaces on a permeable membrane substrate with planar microfabricated electrodes. An RTIL sensor with a 2mm×2mm sensing area is described, and measured responses to methane, a dangerous residential and occupational gas, and sulfur dioxide, a common environmental pollutant, are shown. The reported sensor structure and fabrication process enable realization of sensor arrays for multi-gas monitoring in a low power, miniaturized, wearable system platform.

Keywords – Gas sensor, planar electrode, electrochemical impedance spectroscopy, room temperature ionic liquid

I. INTRODUCTION

Exposure to air toxins and harmful gases is an ever present concern for human health in modern society. Airborne pollutants cause discomfort, illness, and even death[1]. Similarly, as energy demands continue to increase, exposure to explosive gases at home or at work threaten human safety. For example, exposure to sulfur dioxide (SO₂) correlates to an increase in cardiopulmonary mortality, and methane (CH₄) leakage from stoves and boilers in homes are sources of fires and explosions. As these dangers to human health and safety increase, there is a growing need for miniaturized, low power, multi-gas monitoring systems suitable for individuals to wear and capable of constantly examining the surrounding environment. Although numerous efforts have been made to develop gas sensors that can accurately measure air pollutants[2, 3], a low-cost, low-power, real-time, wearable microsystem for gas monitoring that can be widely distributed for biomedical applications is still unavailable.

To realize such a reliable multi-gas monitor in a microsystem platform, a gas sensor array with fast response time, low power consumption, and small footprint is needed.

A promising approach is to utilize an electrochemical sensing methodology[4] with room temperature ionic liquids (RTILs) as the sensing media[5]. When sensing gases, electrochemical methods provide good selectivity with low power consumption and wide dynamic range. The instrumentation needed for such methods can readily be implemented as a single microelectronics chip suitable for portable/wearable systems[6-8]. RTILs are nonvolatile and conductive compounds consisting entirely of ions. With properties such as negligible vapor pressure, wide potential windows, and high thermal stability, RTILs offer a promising electrolyte for robust electrochemical gas sensors that can operate in extreme conditions. In addition, unlike conventional tin dioxide gas sensors that operate at over 200 °C[9], RTILs function at room temperature and thus greatly reduce power demands by eliminating the need to heat the sensor. With electrochemical measurement, RTILs are capable of sensing a variety of gases, including oxygen, combustible gases and ambient toxic gases [10-13].

Our team has recently developed an RTIL-based electrochemical gas sensor that demonstrates high sensitivity and rapid response to methane[14]. This device utilizes a structure of RTIL coating on metal electrodes over a porous polytetrafluoroethylene (PTFE) membrane. This paper reports a fabrication process and gas sensor structure that enables significant miniaturization of the device. Section II introduces the planar-electrodes-on-permeable-membrane (PEoPM) gas sensor structure. Section III presents the microfabrication process for a miniaturized PEoPM gas sensor. Finally test results of a miniaturized gas sensor are shown in Section IV.

II. SENSOR STRUCTURE AND FABRICATION OF MACRO SENSOR

The main obstacle to response time in existing RTIL-based electrochemical gas sensors[10-13] is the slow diffusion of target gases from the RTIL surface to the electrodes. As illustrated in Fig. 1(a), in the conventional sensor structure, the electrodes are fabricated on a substrate and RTIL is then coated on top of the electrodes. Because

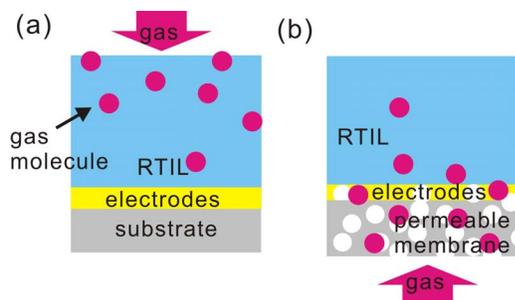


Fig. 1. (a) Conventional sensor structure: response time is slow due to slow gas diffusion through RTIL; (b) electrodes-on-permeable-membrane structure: response time is improved due to fast gas diffusion in the permeable membrane.

the electrochemical reaction happens at the interface of the RTIL and the electrodes, a response cannot be measured until the gas analyte dissolves into the RTIL and reaches the electrodes. A full-scale response to gas analyte is achieved only after an equilibrium forms on the interface. The time interval between the gas reaching the electrodes' surface and establishing equilibrium is primarily dependent upon the gas diffusion speed in the RTIL. Due to RTIL's high viscosity, RTIL-based electrochemical gas sensors suffer low response caused by the slow gas diffusion in the RTIL. By attaching electrodes to a gas-permeable membrane[11] or reducing the RTIL thickness[12], the distance between the RTIL surface and the electrodes can be reduced, thus improving response time. However, these approaches still require the gas to diffuse across the RTIL layer, where diffusion rates are slow. In contrast, the PEOPM structure that bypasses the slow diffusion of gas across the RTIL[14] is illustrated in Fig. 1(b). The electrodes are fabricated directly on a gas-permeable membrane, allowing gas to reach the electrodes/RTIL interface through the permeable membrane, where diffusion is much faster than in the RTIL. To simplify the sensor structure complexity and lower the fabrication cost, working electrodes (WE), counter electrodes (CE) and quasi-reference electrodes (RE) should all be fabricated on the permeable membrane. Using the PEOPM structure, a 5% methane response time of 5s was measured compared to 103s in the case of the traditional structure[14].

In previous work, a macro-scale sensor occupying a 48mm^2 sensing area was fabricated as follows. First, a stainless steel mask was mounted against the porous PTFE and then a gold film was deposited. After removing the mask, patterned planar gold electrodes were formed. Finally, the RTIL was coated on the electrodes to form the sensor. Because RTILs are a highly resistive electrolyte, the sensor electrodes were designed to minimize the electrolyte resistance by interdigitating the WE and CE electrodes and minimizing the gap between them. However, the stainless steel hard mask was prepared by electric discharge

machining (EDM) which only provides a resolution of around $200\mu\text{m}$. Thus the WE-CE gap could not be reduced below $200\mu\text{m}$, which required the electrodes to occupy a large area to keep the gap resistance reasonable. To overcome this significant limitation, the fabrication process described in section III was developed.

III. FABRICATION OF A MINIATURIZED SENSOR

Microfabrication processes has been well developed and widely used in the semiconductor industry. Using photolithography followed by thermal metal deposition and liftoff process, electrode patterns on smooth substrates can easily be formed. Traditional photolithography has a resolution on the order of $1\mu\text{m}$ and should be suitable for fabricating miniaturized gas sensors. However, directly applying traditional photolithography on porous PTFE substrates, as desired here, introduces several problems that require development of a new photolithography process for porous substrates.

First, note that photoresist is generally spin-coated onto a substrate that is vacuum-attached to the spinner. However, porous PTFE is soft and cannot be reliably held by vacuum because it is porous. A preliminary experiment demonstrated that, when a PTFE sheet was put directly on the spinner, significant photoresist would be sucked into the PTFE and could not be removed during liftoff. To resolve this problem, the porous PTFE was clamped to a glass substrate, and the glass was placed on the spinner and held by vacuum.

Second, because porous PTFE has a rough surface, standard photoresist coatings of PTFE are not reliably smooth enough for patterning. For example, with porous PTFE having a $4\mu\text{m}$ pore size, around $4\mu\text{m}$ of surface roughness can be expected. To resolve this problem, a thick film photoresist was selected. Hoechst AZ4620 was spin-coated at 2100rpm to create $10\mu\text{m}$ thick layer. Lithography by 60s UV exposure and 300s developing in AZ300 MIF developer was found to reliably remove the thick resist. The profile scan by a Dektak3 Surface Profiler in Fig. 2 demonstrates that the photoresist AZ4620 covered the rough surfaces of porous PTFE and that a good edge step, suitable for liftoff, was formed.

Third, note that preliminary experiments found metal liftoff to be difficult, even after a gold-deposited sample was soaked in acetone for several days. One possible reason is that the photoresist became polymerized during the half hour physical vapor deposition, where the temperature on the sample is over 100°C . Because polymerized photoresist cannot easily be dissolved in acetone, this would cause the liftoff to failure. To solve this problem, note that exposure to UV should prevent photoresist from polymerizing. Thus,

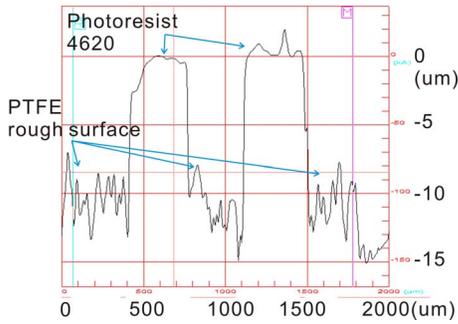


Fig. 2. Profile scan by Dektak3 Surface Profiler. The photoresist AZ4620 covered the rough surface of porous PTFE and a good step was formed.

a 60s flood exposure was performed after developing the photoresist and before metal deposition.

Finally, because of the uneven distribution of pores on PTFE surface, the conductivity of metal traces were found to be unreliable and in the worst case could result in entire electrode fingers being disconnected, resulting in significant device-to-device variation. To resolve this problem, one possible solution is to increase the width of the electrodes thereby reducing the chance of a discontinuity. However, this approach conflicts with the goal to miniaturize the device. To analyze the relation between device variation and electrode width, 4 groups of 10mm-long gold traces with different widths were fabricated. Each group had eight identical elements, and resistance values were measured to compare their average sheet resistance and standard deviation as shown in Table I. As expected, the results show that traces with larger widths have better consistency. 200 μm width was chosen as a compromise between reliability and the miniaturization goal.

By addressing each of the challenges described above, the RTIL gas sensor fabrication process was optimized to achieve a miniaturized PEoPM structure. The fabrication process is illustrated in Fig. 3. POREX® porous PTFE with 35% porosity and 4 μm pore size (Zitex TM, Chemplast, Incorporated, Wayne, New Jersey) was chosen as the permeable membrane due to its excellent inertness and hydrophobic response to the RTIL. Gold was chosen as the electrode material because it is highly inert and can be

TABLE I
AVERAGE SHEET RESISTANCE AND STANDARD DEVIATION WITH DIFFERENT WIDTH CONFIGURATIONS

| width (μm) | average (Ω) | standard deviation (Ω) | standard deviation (%) |
|-------------------------|----------------------|---------------------------------|------------------------|
| 100 | 0.288 | 0.044 | 15.2 |
| 200 | 0.323 | 0.041 | 12.7 |
| 400 | 0.327 | 0.034 | 10.3 |
| 800 | 0.306 | 0.023 | 7.5 |

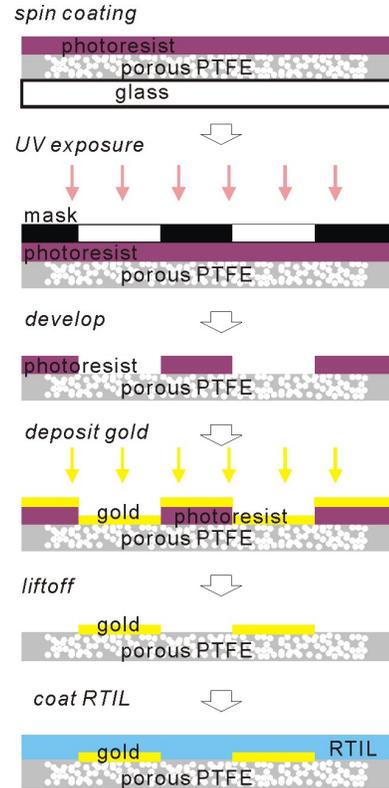


Fig. 3. Miniaturized RTIL-based PEoPM sensor fabrication process.

readily deposited in thin films and patterned in a planar process. High-purity RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{mpy}][\text{NTf}_2]$) was chosen as the electrolyte due to its low viscosity and high chemical stability.

The porous PTFE sheet was clamped on glass wafer and spin-coated by AZ4620 photoresist. 5min soft bake at 95 $^\circ\text{C}$ was performed, followed by a 60s UV exposure through the electrode pattern mask. After 300s developing in AZ300 MIF developer, the sample was flood exposed for 60s. Then a 300nm-thick gold film was deposited on the porous PTFE sheet using physical vapor deposition (PVD, Edward 360 thermal evaporator). After deposition, the sample was soaked in acetone overnight and the gold electrodes pattern was formed by liftoff. Finally, to add the RTIL interface, the electrodes were then coated with 200 μm -thick $[\text{C}_4\text{mpy}][\text{NTf}_2]$ with a droplet process.

IV. RESULTS

Following the microfabrication process above, the miniaturized PEoPM device shown in Fig. 4 was fabricated. The electrode structure occupies a 2mm \times 2mm sensing area, only 8% of the area in the macro-scale device. WE and CE were interdigitated for impedance measurement with a 200 μm width and a 100 μm gap, and an RE was included to improve electrochemical stability. An o-ring was used to

separate the sensing electrode area from the connection pads during testing.

The fabricated sensor was placed in a gas chamber and sealed with the o-ring. Electrochemical impedance spectroscopy (EIS) tests were performed with a VersaStat MC potentiostat (Princeton Applied Research, Oak ridge, TN, U.S.A.) using a 10mV peak-to-peak sinusoidal signal.

To demonstrate the functionality of the microfabricated PEOPM device, CH₄ and SO₂ were selected as example pollutants. The sensor was exposed to CH₄ and SO₂ individually, and the impedance spectra were recorded. CH₄ concentration was varied from 0 to 5% because 5% is the lower explosive limit for CH₄; and SO₂ concentration was varied from 0 to 5ppm because 5ppm is the permissible exposure limit for SO₂. Impedance amplitude values at 1Hz were extracted to form the CH₄ and SO₂ calibration curves. Fig. 5 plots the normalized difference between the response and baseline (0% CH₄/SO₂) impedances, $\Delta|Z|$, versus CH₄/SO₂. The results demonstrate good sensitivity over the range of interest. In fact, the CH₄ sensitivity of the miniaturized device is comparable to the macro-scale device [14] even though it is more than 10 \times smaller. This miniaturized sensor is thus well suited to measure multiple gases in a wearable real-time gas monitoring microsystem.

V. CONCLUSION

This paper introduced a microfabrication process for a miniaturized RTIL-based gas sensor featuring a planar-electrode-on-permeable-membrane structure that provides a

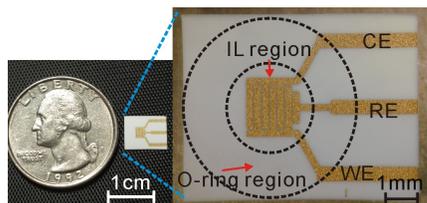


Fig. 4. Photograph of fabricated miniaturized PEOPM device. The WE and CE are interdigitated with finger gaps of 100 μ m. The o-ring isolates the RTIL area from the contact pads.

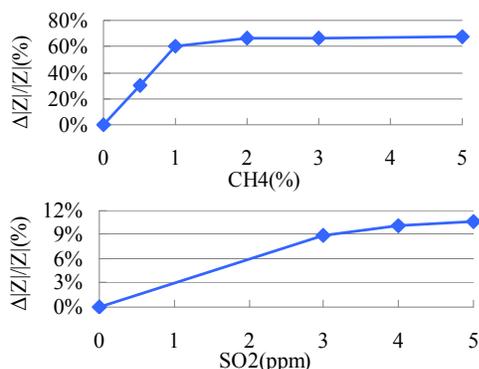


Fig. 5. CH₄ and SO₂ calibration curve for RTIL sensor from EIS test data at 1Hz.

fast path for gas to diffuse to the active sensor electrode area. Process challenges were addressed and tradeoffs were analyzed. Using CH₄ and SO₂ as an example gases relevant to human health and safety, the sensor's functionality was demonstrated. The sensor achieves the goals of small size, low power, low cost, and fast response. The reported microfabrication process enables future realization of miniaturized sensor arrays for wearable multi-gas monitoring microsystems.

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REFERENCES

- [1] R. D. Brook, "Cardiovascular Effects of Air Pollution," *Clinical Science*, vol. 115, pp. 175-187, 2008.
- [2] N. Yamazoe, "Toward Innovations of Gas Sensor Technology," *Sensors and Actuators B: Chemical*, vol. 108, pp. 2-14, 2005.
- [3] P. Aragón, J. Atienza, and M. D. Climent, "Analysis of Organic Compounds in Air: A Review," *Critical Reviews in Analytical Chemistry*, vol. 30, pp. 121-151, 2000.
- [4] J. R. Stetter, G. Korotcenkov, X. Zeng, Y. Tang, and Y. Liu, "Electrochemical Gas Sensors: Fundamentals, Fabrication, and Parameters," in *Chemical Sensors Comprehensive Sensor Technologies*, vol. 5, G. Korotcenkov, Ed., ed New York: Momentum Press, 2011, pp. 1-89.
- [5] M. C. Buzzeo, C. Hardacre, and R. G. Compton, "Use of Room Temperature Ionic Liquids in Gas Sensor Design," *Analytical Chemistry*, vol. 76, pp. 4583-4588, 2004.
- [6] A. Manickam, A. Chevalier, M. McDermott, A. D. Ellington, and A. Hassibi, "A CMOS Electrochemical Impedance Spectroscopy (EIS) Biosensor Array," *IEEE Transactions on Biomedical Circuits and Systems*, vol. 4, pp. 379-390, 2010.
- [7] P. M. Levine, G. Ping, R. Levicky, and K. L. Shepard, "Active CMOS Sensor Array for Electrochemical Biomolecular Detection," *IEEE Journal of Solid-State Circuits*, vol. 43, pp. 1859-1871, 2008.
- [8] Y. Chao, S. R. Jadhav, R. M. Worden, and A. J. Mason, "Compact Low-Power Impedance-to-Digital Converter for Sensor Array Microsystems," *IEEE Journal of Solid-State Circuits*, vol. 44, pp. 2844-2855, 2009.
- [9] J. Watson, K. Ihokura, and G. S. V. Coles, "The Tin Dioxide Gas Sensor," *Measurement Science and Technology*, vol. 4, p. 711, 1993.
- [10] X.-J. Huang, L. Aldous, A. M. O'Mahony, F. J. del Campo, and R. G. Compton, "Toward Membrane-Free Amperometric Gas Sensors: A Microelectrode Array Approach," *Analytical Chemistry*, vol. 82, pp. 5238-5245, 2010.
- [11] Z. Wang, P. Lin, G. A. Baker, J. Stetter, and X. Zeng, "Ionic Liquids as Electrolytes for the Development of a Robust Amperometric Oxygen Sensor," *Analytical Chemistry*, vol. 83, 2011.
- [12] M. A. G. Zevenbergen, D. Wouters, V.-A. T. Dam, S. H. Brongersma, and M. Crego-Calama, "Electrochemical Sensing of Ethylene Employing a Thin Ionic-Liquid Layer," *Analytical Chemistry*, vol. 83, pp. 6300-6307, 2011.
- [13] N. Dossi, *et al.*, "An Electrochemical Gas Sensor Based on Paper Supported Room Temperature Ionic Liquids," *Lab on a Chip*, vol. 12, 2012.
- [14] Z. Wang, X. Mu, M. Guo, Y. Huang, A. J. Mason, and X. Zeng, "Ionic Liquid Double Layer Capacitor: Quantitative Evaluation of Methane Adsorption at the Ionic Liquid Electrified Metal Interface," *Analytical Chemistry*, in review.