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Photopatternable Polymeric Membranes for Optical Oxygen Sensors

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Abstract

A new class of optical oxygen sensor that can be photopatternable by traditional UV lithography is presented. They are fabricated using photopatternable spin-on silicone (polydimethyl-siloxane, PDMS) with oxygen sensitive luminescent dyes. It has a good adhesion property and can be applied on glass or on photopolymer (SU-8) without any additional surface treatments. The optimum mixture composition for patternable oxygen sensitive membranes is investigated and its optical properties are characterized. Proof-of-concepts for two applications, intensity-based oxygen sensing with SU-8 based structure and self-calibration fluidic oxygen sensor, are described. These photopatternable optical membranes will find many applications wherever small patterns of oxygen sensitive membranes are required.

Index Terms

Fluidics; oxygen; porphyrin; ruthenium; silicone

I. Introduction

Determination of oxygen concentration is very important in many environmental, medical, and clinical applications. One popular type of oxygen sensor is the optical oxygen sensor because they offer a lot of advantages compared to its electrochemical counterpart, such as no electrical interference, no oxygen consumption, and compatibility with imaging. Most of the optical sensors are based on the principle that oxygen quenches the luminescence emitted from the luminescent dyes which are immobilized in an oxygen permeable membrane such as silicone [1]–[4].

In many applications of bio-MEMS devices, there is a large need of microscopically patterned optical membranes to measure chemical parameters in a small local area. Most of the oxygen sensitive membranes are, however, nonpatternable by photolithography and very little progress has been made towards producing patternable optical membranes. For this work to be possible, a membrane matrix material is needed that is transparent, oxygen-permeable, and photopatternable.

In this report, an effort has been made to produce small patterns of thin oxygen sensitive membranes using photopatternable silicone [5]. To our best knowledge, this is the first report of using photopatternable silicone for chemical sensing applications. We investigated optimum mixture composition for patternable oxygen sensitive membranes and its optical properties were characterized. There are two applications that prompted us to produce photopatternable oxygen sensitive membranes. Our first application is oxygen sensors on SU-8 structures in a chip. SU-8 is an epoxy-based, negative tone, high aspect ratio photoresist that has excellent optical properties useful for chemical sensing [6]–[8]. Attaching chemically sensitive membranes on the surface of SU-8 serving as the structuring material for fluidic channels or waveguides enables very attractive optical sensing applications [9]. The second application is a self-calibration fluidic oxygen sensor [10], wherein the patterned oxygen sensitive membrane is located inside the fluidic channel. New integration processes of patterning oxygen sensitive membranes for intensity-based chemical sensors were described.

II. Experiments

A. Preparation of Patternable Oxygen Sensor Membranes

Two oxygen sensitive luminescent dyes were used for the preparation of oxygen sensor membranes. One was a phosphorescent dye, platinum porphyrin and the other was a fluorescent dye, ruthenium complex. The oxygen sensor membranes using these dyes were prepared as follows.

Platinum porphyrin complex, Pt (II) meso-tetra(pentafluorophenyl) porphine (Frontier Scientific) was used for this study. A photopatternable spin-on silicone (WL-5150, Dow Corning) was used as the matrix to immobilize porphyrin. Since platinum porphyrin was soluble in silicone, it could be evenly dispersed in the silicone. First, a small amount of platinum porphyrin was dissolved in 0.3 ml toluene in a glass container and stirred for 10 min. Then, 3.3 ml of WL-5150 (photopatternable silicone) was added and stirred for 30 min.

Ruthenium complex, dichlorotris (1,10-phenanthroline) ruthenium (II) hydrate 98% (Sigma Aldrich) was the oxygen sensitive fluorescent compound used for this study. The same photopatternable spin-on silicone was used as the matrix to immobilize the ruthenium. Since ruthenium was not soluble in silicone, it was first loaded onto fumed silica particles (Cab-O-Sil Fumed silica EH-5, Mozel Inc.) and then the loaded silica particles were evenly dispersed in the silicone [2]. A small amount of ruthenium complex was dissolved in 10 ml ethanol in a glass container and stirred for 30 min. 0.70 g of silica was added to the container and stirred for 24 h. The silica particles, which were initially white in color, became yellow and the ethanol solution became very pale, thus providing evidence that most of the ruthenium has been loaded onto silica particles. The mixture was allowed to dry for 12 h, and then the container was placed in a vacuum chamber to ensure that the ethanol was completely evaporated. Now, the dried ruthenium-loaded silica was mixed with 6.6 ml of photopatternable silicone. Photopatternable silicone is viscous at room temperature and, hence, it is difficult to mix it with silica. Therefore, 0.6 ml of toluene was added to the mixture and was stirred again for 24 h to ensure that the silica is evenly dispersed in silicone.

B. Fabrication of Oxygen Sensors on Glass and SU-8 Surfaces

The photopatternable oxygen sensitive membranes on bare glass were prepared, as in Fig. 1, as a preliminary step to find the optimum membrane composition. A standard 4-inch glass wafer was cleaned by immersing it in acetone, methanol and DI water each for 3 min as per the standard cleaning procedure. The wafer was then dehydrated at 200 °C for 15 min on a hot plate. A layer of patternable oxygen sensing mixture was spin coated at 500 rpm for 40 s to obtain a thickness of about 35 μm . It was then subjected to soft bake at 70 °C for 2 min and at 110 °C for 4 min. UV exposure was done for an energy dose of 1 350 mJ/cm^2 (5.5 mW/cm^2 at 365 nm for 245 s). Post exposure bake was done at 150 °C for 150 s. Patternable oxygen sensing membrane was developed using negative resist developer (NRD, Air Products), then followed by a hard bake at 140 °C for 3 min.

Fig. 2 shows the fabrication process of oxygen sensor membrane on SU-8 based structure. A glass wafer was cleaned and dehydrated as per the standard cleaning procedure. An anti-reflective coating (DARC 300, Brewer Science) was then spin coated at 1000 rpm for 90 s to achieve a thickness of 1.2 μm . DARC 300 was used to minimize any possible interference from adjacent SU-8 structure and also to enhance the vertical side-wall profile of SU-8. DARC 300 is not photosensitive but it can be patterned when used in conjunction with positive photoresist. After spin coating DARC, it was soft baked at 80 °C and β -baked at 150 °C, each for 1 min. Positive photoresist (S1813, Shipley) was then spin coated on the existing DARC at 2000 rpm for 90 s. Soft baking was done at 115 °C for 1 min, and then followed by UV exposure at an energy dose of 150 mJ/cm^2 (8.0 mW/cm^2 at 436 nm for 19s) with a mask. After exposure, S1813 developer (Rohm and Haas Electronic Materials) was used to develop both S1813 and the underlying DARC simultaneously. DARC patterns were obtained by stripping S1813 followed by a hard bake at 225 °C for 5 min.

SU-8 2050 (MicroChem) was then spin coated at 2000 rpm for 30 s to achieve a thickness of about 75 μm . Soft baking was done at 65 °C for 3 min and at 90 °C for 10 min. The same mask was aligned and exposed for an energy dose of 210 mJ/cm^2 (5.5 mW/cm^2 at 365 nm for 38 s). After exposure, post exposure bake was done at 65 °C for 2 min and at 90 °C for 8 min. With the SU-8 left undeveloped, a layer of patternable oxygen sensing mixture was spin coated and patterned as described previously except the exposure procedure. As the exposure time for silicone is long, cycles of 30 s exposure and rest time of 1 min was repeated to avoid possible adverse effects of overexposing SU-8. Finally, SU-8 was developed using SU-8 developer. The final fabricated structure is as shown in Fig. 2(h). One of the advantages of this fabrication procedure is that the same mask can be used for all the three photopolymers.

C. Fabrication of Self-Calibration Fluidic Oxygen Sensor

Fig. 3 shows the fabrication process of self-calibration fluidic oxygen sensor. The substrate was a silicon wafer with a silicon nitride coating as an insulating layer. A platinum/titanium thin film was deposited by e-beam evaporation and patterned by liftoff technique to define the electrodes. A PDMS sheet (750 μm thick) was prepared by spin-coating and curing on a silicon wafer to serve as a spacer layer. A channel of 2.5 $\text{cm} \times 1.75 \text{ mm}$ was made within the PDMS sheet by a surgical blade. The PDMS sheet was attached to the substrate by simply pressing on it to seal the interface between the sheet and the silicon nitride layer. Inlet and outlet holes were drilled in a glass slide. Then, an oxygen sensitive membrane was patterned on it as described earlier and flipped over the channel. The electrodes within the microchannel are used in electrolysis of sample solution generating oxygen and hydrogen bubbles, which serve as the calibrants for *in situ* two-point self-calibration of the oxygen sensor [10].

D. Instrumentation

The luminescence intensity measurements were performed, as shown in Fig. 4. A spectrofluorometer (USB2000-FLG, Ocean optics) was used as the detector. Since the excitation wavelength of ruthenium complex and porphyrin are different, two different light-emitting diodes (LEDs) (LS450 and LS380, Ocean Optics) were used as the light source. A reflection probe (R400-7-UV-VIS, Ocean Optics), consisted of a bundle of illumination and read fibers, was connected between the LED and the spectrometer. The common end was placed in close proximity to the sample which was placed inside a container. By adjusting the oxygen and nitrogen gas flows through the mass flow controllers, different oxygen concentrations were obtained inside the container. The read fiber captures luminescence and was high-pass filtered (>540 nm) before it was read by the spectrometer. The spectrometer was connected to the computer and the spectrum was displayed.

III. Results and Discussion

A. Platinum Porphyrin Membrane on Bare Glass

Pt (II) meso-tetra(pentafluorophenyl) porphyrin was first dissolved in toluene and the excitation and emission wavelengths were found to be 390 nm and 644.59 nm, respectively. The excitation and emission spectra of porphyrin in photopatternable silicone is shown in Fig. 5(a). The emission peak is at 644.59 nm, same as that of platinum porphyrin dissolved in toluene. This implies that platinum porphyrin emission wavelength is not affected by photopatternable silicone.

For the optimization of composition, several mixtures of different concentrations of platinum porphyrin in patternable silicone were spin coated on glass wafer. I_0/I versus the oxygen concentration (i.e., the Stern–Volmer plots) for different platinum porphyrin concentrations are plotted in Fig. 5(b). It is evident that higher the platinum porphyrin concentration, higher is the sensitivity. Concentrations of 1.70, 0.51, and 0.25 mM showed good sensitivity towards a wide range of oxygen concentrations but were not patternable. Concentrations of 0.08 and 0.01 mM, however, did not exhibit any significant sensitivity although they could be patterned photolithographically. Fig. 5(c) shows a 250 μm diameter (35 μm thick) circular pattern of 0.08 mM concentration on bare glass. Thus, it was not possible to produce patternable phosphorescent membranes with satisfactory sensitivity using platinum porphyrins in patternable silicone. All or most of the membranes with higher porphyrin concentration was wiped out while developing, leading to poor patterning. The plausible reason for this could be that the exposure wavelength for patternable silicone (365 nm) was close to excitation wavelength of platinum porphyrin (390 nm). At higher porphyrin concentrations, significant UV energy was exhausted for the excitation of porphyrin, thus affecting the crosslinking of photopatternable silicone. Our next effort would be to use other porphyrins whose excitation wavelengths does not interfere with the exposure wavelength of photopatternable silicone.

B. Patterned Ruthenium Complex Membrane on Bare Glass

The excitation and emission spectra of dichlorotris (1,10-phenanthroline) ruthenium (II) hydrate 98% in photopatternable silicone is shown in Fig. 6(a). The emission peak is at 589.90 nm, which is the same as that of ruthenium complex dissolved in ethanol. This implies that ruthenium emission wavelength is not affected by photopatternable silicone and fumed silica as in a previous report [2].

The sensor mixture composition was optimized with respect to the patternability, which largely depends on the amount of silica and toluene in silicone. Small amount of silica in silicone lead to small sensitivity whereas large amount of silica blocked or minimized the crosslinking leading to poor patternability. Likewise, small amount of toluene in silicone makes mixing

difficult, whereas large amount of toluene diluted silicone leading to poor patternability, respectively. After extensive experiments using silica in 0.5–0.9 g range and toluene in 0.3–0.9 ml range, 0.7 g of silica and 0.6 ml of toluene were found to be the optimized amounts that could be mixed with silicone to obtain satisfactory patternability.

For the optimization of ruthenium content in silicone, several mixtures of different concentrations were patterned on glass wafer. I_0/I versus the oxygen concentration for different ruthenium concentrations are plotted in Fig. 6(b). It is evident that higher the ruthenium concentration, higher is the sensitivity. There is, however, a maximum amount of ruthenium that can be adsorbed on silica. Above this, the extra ruthenium which is not loaded on silica is likely to remain in silicone as clusters since ruthenium is not soluble in silicone. This nonuniform distribution of ruthenium causes higher nonlinearity in the Stern–Volmer plot [3]. I_0/I_{100} (i.e., the sensitivity at 100% oxygen) versus the ruthenium concentration is also plotted in Fig. 6(c). Increasing ruthenium concentration above 0.80 mM barely increases the sensitivity as self-quenching becomes severe [4]. Among these, the sensitivity of 0.80 mM was the highest with a better linearity and it was chosen as the optimum concentration of ruthenium in silicone.

C. Application I: Oxygen Sensor With SU-8 Based Structure

Ruthenium complex was immobilized in silicone and patterned on the top of each SU-8 based structure of same height. The glass surface not covered by SU-8 was blocked with a black anti-reflective opaque coating. The ruthenium complex emits fluorescence depending on the oxygen concentration and sends light back through the SU-8 “vertical waveguide” to the detector below the glass wafer. The detector such as CCD camera can thus capture the image of the oxygen concentration from the waveguide array. It is considered that this platform exhibits a high possibility to achieve three dimensional optical oxygen imaging utilizing novel structures such as SU-8 pillar array based on multiple layer photolithography [11]. In this phase of proving the concept, however, optical properties of each sensor were individually characterized. The diameter of SU-8 structure was kept rather large (2 mm) for easy measurement with the reflection probe. However, typically 100 μ m wide silicone/SU-8 structure have been successfully prepared by this fabrication protocol, as shown in Fig. 7(a).

Based on the preliminary characterization with the samples on bare glass, the photopatternable silicone membrane, i.e., 0.80 mM was patterned on SU-8 layer. From Fig. 7(b), the emission peak of ruthenium complex on SU-8 layer is also 589.90 nm as expected. The Stern–Volmer plot of the oxygen sensing membrane on SU-8 is plotted in Fig. 7(c) and was compared with that on the glass. The sensitivity decreased from 3.17 on glass to 2.32 on SU-8. This could be due to the attenuation caused by the SU-8 layer. The time response of oxygen sensitive membrane is shown in Fig. 7(d). It can be noticed that the response from low to high concentration of oxygen is much faster than that from high to low concentration. It is considered that the diffusion of oxygen into the membrane is fast (about 60 s for 90% response from 21 % to 100% oxygen), but removal of oxygen from the membrane takes longer time (about 160 s for 90% response from 100% to 0% oxygen). A sensitivity of 2.32 (I_0/I_{100}) and a signal-to-noise ratio of 19.4 ($I_{100} = 485$ counts, noise = 25 counts) is good to be used as an oxygen sensor. Another observation is that the patterned oxygen sensor did not exhibit any recognizable photobleaching after about 10 h of cumulative LED illumination.

D. Application II: Self-Calibration Fluidic Oxygen Sensor

A self-calibration fluidic oxygen sensor was fabricated as explained previously. The inlet and outlet holes allow the samples to flow in and out of the microchannel. Fig. 8(a) shows the measurements of samples with different oxygen concentrations, both gaseous and dissolved phases. For dissolved oxygen measurements, phosphate buffer solutions (pH 7.4, 10 mM) were

first saturated with different oxygen concentrations in a beaker and then transferred to the fluidic channel. The electrode pair within the microchannel electrolyzes the solution to generate a pair of oxygen and hydrogen bubbles at each electrode depending on their polarity. These bubbles serve as calibrants for *in situ* two-point self-calibration of the oxygen sensor [10]. The generated bubble was shifted to enclose the oxygen sensitive membrane. The fluorescence intensity measurements were then taken. Since this on-chip oxygen self-calibration method is still in the proof-of-concept phase, the exact oxygen concentrations within these bubbles are not known. It is assumed that the generated oxygen and hydrogen bubbles are 100% (i.e., I_{100}) and 0% (i.e., I_0) oxygen microenvironments, respectively. These two data points for oxygen and hydrogen bubbles in Fig. 8(a) exhibit good agreement with gaseous and dissolved phase data. Time response is shown in Fig. 8(b) that is continuous recording of the movement of bubbles within the channel. The time response shows a similar trend with that of Fig. 7(d) in that the diffusion of oxygen into the membrane is faster (about 40 s for 90% response from 21% solution to presumably 100% oxygen bubble) than the removal from the membrane (about 75 s for 90% response from 21% solution to presumably 0% hydrogen bubble). The results imply that the patternable sensor membrane is a promising optofluidic integration process that can be employed in the future development of integrated calibration module to achieve the on-chip, on-demand, and *in situ* self-calibration functionality.

IV. Conclusion

We have presented a new class of optical oxygen sensors that can be photopatternable by traditional UV lithography. The photopatternable silicone proved to be a good candidate material for patterning luminophores for optical sensing applications. The composition of oxygen sensing mixture has been optimized and can be directly used to make oxygen sensitive patterns. Because of its good adhesion properties, it can be prepared on glass surfaces or on chemically inert photopolymers such as SU-8 without additional surface treatment. Proof-of-concepts for two applications, intensity-based oxygen sensing with SU-8 based structure and self-calibration fluidic oxygen sensor have been demonstrated. This type of membrane is anticipated to make viable integrated components of waveguide-based chemical microsensors such as planar type evanescent sensors and vertical type reflectance sensors. This new integration process will find many other applications wherever small patterns of oxygen sensitive membranes are required in both intensity-based and lifetime-based optical sensors.

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Biographies

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Fig. 1.
Fabrication of photopatternable oxygen sensitive membrane array on bare glass.

Fig. 2.
Fabrication of photopatternable oxygen sensitive membrane array on SU-8 based structures.

Fig. 3.
Fabrication of self-calibration fluidic oxygen sensor.

Fig. 4.
Luminescence measurement setup.

Fig. 5.

Optical properties of platinum porphyrin layers on bare glass. (a) Excitation and emission spectra of platinum porphyrin in patternable silicone on bare glass. (b) Stern–Volmer plots versus gaseous oxygen with different porphyrin concentrations in silicone membranes (not patterned). (c) Typical 250 μm diameter circular pattern of 0.08 mM concentration on bare glass.

(a)

(b)

(c)

Fig. 6.

Optical properties of patterned ruthenium complex membranes on bare glass. (a) Excitation and emission spectra of ruthenium complex in patterned silicone on bare glass. (b) Stern-Volmer plots versus gaseous oxygen with different ruthenium concentrations in patterned silicone membranes (2 mm diameter) on bare glass. (c) I_0/I_{100} versus ruthenium complex concentration in patterned silicone membrane on bare glass.

Fig. 7.

Optical properties of patterned ruthenium complex membranes on SU-8 layer. (a) Typical 100 μm diameter patterned ruthenium membrane on SU-8. (b) Excitation and emission spectra of ruthenium complex in patterned silicone on SU-8 layer. (c) Stern–Volmer plots versus gaseous oxygen with patterned silicone membranes (2 mm diameter) on SU-8 layer and on bare glass. (d) Time response to gaseous oxygen.

(a)

(b)

Fig. 8. Optical properties of patterned ruthenium complex membrane in fluidic channel. (a) Stern–Volmer plots of patterned silicone membrane in gaseous, dissolved oxygen environments, and in bubbles. In each case, oxygen percentage refers to amount of oxygen contained in the gaseous phase. Dissolved oxygen is considered at equilibrium with this phase. (b) Time response to dissolved oxygen with self-calibration fluidic oxygen sensor.