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Contact CMOS imaging of gaseous oxygen sensor array

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Abstract

We describe a compact luminescent gaseous oxygen (O₂) sensor microsystem based on the direct integration of sensor elements with a polymeric optical filter and placed on a low power complementary metal-oxide semiconductor (CMOS) imager integrated circuit (IC). The sensor operates on the measurement of excited-state emission intensity of O₂-sensitive luminophore molecules tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) ([Ru(dpp)₃]²⁺) encapsulated within sol-gel derived xerogel thin films. The polymeric optical filter is made with polydimethylsiloxane (PDMS) that is mixed with a dye (Sudan-II). The PDMS membrane surface is molded to incorporate arrays of trapezoidal microstructures that serve to focus the optical sensor signals on to the imager pixels. The molded PDMS membrane is then attached with the PDMS color filter. The xerogel sensor arrays are contact printed on top of the PDMS trapezoidal lens-like microstructures. The CMOS imager uses a 32 × 32 (1024 elements) array of active pixel sensors and each pixel includes a high-gain phototransistor to convert the detected optical signals into electrical currents. Correlated double sampling circuit, pixel address, digital control and signal integration circuits are also implemented on-chip. The CMOS imager data is read out as a serial coded signal. The CMOS imager consumes a static power of 320 μW and an average dynamic power of 625 μW when operating at 100 Hz sampling frequency and 1.8 V DC. This CMOS sensor system provides a useful platform for the development of miniaturized optical chemical gas sensors.

Keywords

Contact imaging; CMOS imager; Xerogel thin-films; Gas sensors; O₂ sensors; Optical sensors; Luminescence; PDMS; Microlens

1. Introduction

Miniaturized chemical sensors continue to play an important role in patient bed-side monitoring, implantable microsensors, disposable sample-to-answer systems, and personal safety [1,2]. Many research groups are pursuing research activities to develop sensor systems by integrating the various optical, electrical, fluidic, and biological components into

compact and miniaturized sensors [3–5]. We focus on luminescence sensor microarrays which offer several advantages including fast response, they do not poison sample media, and they require no additional reagents [6]. Sensor microarrays consist of an ordered assembly of microscale elements that each contains different or identical immobilized recognition element and allow one to multiplex and de-multiplex biological or chemical information from multi-component samples. Further, sensor microarrays would provide simultaneous multiple independent sensor responses which would allow incorporation of sensor redundancy, artificial intelligence tools [7], and improving the reliability of sensor systems against changes in ambient conditions such as temperature [8].

Luminescence based sensors require an optical excitation source for exciting the sensor materials with electromagnetic radiation and a photodetector component for monitoring the excited state emission response from the sensor materials at a higher wave-length electromagnetic spectrum that is filtered from the excitation input [9]. As the photodetector component, complementary metal-oxide semiconductor (CMOS) imagers are preferable to convert the optical signals into electrical signals because of monolithic integration of photodetection elements and signal processing circuitry leading to low cost miniaturized systems [10]. CMOS imager integrated circuits (ICs) have been used for many luminescence applications, starting with Vo-Dinh [11] who reported a CMOS phototransistor based imager to implement a microsystem for DNA microarrays. Subsequent works were related to DNA microarrays [12,13], modeling and simulation [14], and excited-state lifetime measurements [15]. There are previous reports from several groups on the use of discrete CMOS photodetectors for luminescence monitoring in biochemical sensors [16–21]. More recently, our group proposed chemical sensor microarrays by integration sol–gel derived xerogel sensor microarrays with custom-designed CMOS imager ICs [8,22]. Finally, there have been previous reports of compact optical system integration approaches with poly(acrylic acid) filters integrated with custom-designed CMOS imager ICs to detect fluorescent micro-spheres [23] and imaging of fluorophore-labeled cell cultures [24].

Also, many different approaches have been used to fabricate sensor microarrays including pin [25], contact [26], ink-jet and screen printing [27,28], and photolithography [29]. Here, we use contact printing of xerogel thin films, which serve as immobilization media for sequestering the well-known O₂ responsive luminophore tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) ([Ru(dpp)₃]²⁺), on lens-like structures molded in polydimethylsiloxane (PDMS) substrates. We focus on O₂ sensors as they are well developed and their operation is well understood. Further, O₂ sensors have important uses in many medical, industrial, and scientific applications [30]. Xerogels are porous glasses and their appeal for chemical recognition elements derives from their production at room temperature, thermal stability, tunable pore dimensions and distributions, biocompatibility, adjustable pH, and a broad optical transparency window [31–35]. The O₂ sensors described here operate on the principle of luminescence quenching with O₂ molecules acting as the quencher, *Q* [9]. Thus, one can write the quencher-dependent response, also known as Stern–Volmer equation as,

$$\frac{I_0}{I} = (1 + K_{SV}[Q]) = 1 + k_q\tau_0[Q] \quad (1)$$

where K_{SV} is the Stern–Volmer constant, τ_0 is the excited-state luminescence lifetime for the luminophore in the absence of quencher, Q ; k_q is the bimolecular quenching constant; and I_0 and I are the luminescence intensity in the absence and presence of quencher (O₂).

Polydimethylsiloxane (PDMS) is a silicone-based organic polymer that is soft, flexible, biocompatible and optically transparent and, thus, is well suited to fabricate lenses, filters,

diffusers and other components for optical sensors [36]. PDMS can be doped with apolar hydrophobic color dyes such as Sudan-I, -II or -III to form optical filters that work in different regions of visible electromagnetic spectrum [37]. In the current work, we describe a prototype compact optical gaseous O₂ sensor microsystem using xerogel based sensor elements that are contact printed on top of trapezoidal lens-like microstructures molded into PDMS and combined with another PDMS film that is doped with Sudan-II dye. The integrated structure with xerogel sensor-PDMS films is then carefully aligned and placed on top of a CMOS imager IC. We also describe an ultra-thin packaging scheme for the CMOS imager to maintain the total thickness of the integrated sensor to less than 2 mm. Fig. 1 shows the sensor system block diagram. In this article, Section 2 describes the design and characterization of CMOS imager IC and ultra-thin packaging of the imager. Section 3 describes the fabrication of xerogel sensor materials. Section 4 describes the fabrication of PDMS lenses, filters, and sensor system integration. Finally, Section 5 provides the O₂ sensor measurement results and discussion.

2. CMOS imager IC

The developed CMOS imager IC (Fig. 2) consists of three circuit blocks: (i) active pixel array, (ii) digital control circuit and X–Y address circuit, and (iii) analog signal processing circuit. The imager uses an active pixel sensor (APS) array based on standard circuit designs [38]. Fig. 3 shows the microphotograph of the fabricated 1.5 mm × 1.9 mm CMOS imager IC in TSMC 0.18 μm-CMOS process available through Canada Microelectronics Corporation (www.cmc.ca). The imager design and electrical characterization is extensively detailed in our earlier publication [8]. To operate the APS array, three digital control signals are required: *RST*, *S_x* and *S_y*. The output signal of pixel array is read out serially at *V_{arrayout}* by the signal processing circuit. The signal processing circuitry mainly includes the correlated doubling sampling (CDS) circuit and integrator circuit. The CDS block is used to minimize the fixed pattern noise (FPN) and the integrator is used to integrate the ramp shaped signal into DC form for serial readout. Three digital signals are needed to operate the signal processing circuit: *RST*, *SH*, and the complementary signal of *SH*. All the required digital signals in the imager IC are generated on-chip by the digital control circuit and X–Y address circuit and are synchronized with the external clock signal, *CLK*.

The imager IC includes a 32 × 32 array (1024 elements) of APSs. Each APS pixel uses a vertical p-n-p phototransistor as the photo-detector. Phototransistors can produce current levels that are several times larger in comparison to comparably sized photodiodes. The vertical p-n-p phototransistor can only be used in an emitter-follower configuration and it is formed by the p-active (emitter)/n-well (base)/p-substrate (collector) [16]. Each APS element contains the phototransistor and four MOSFETs (*M_{rs}*, *M_{rd}*, *M_x* and *M_y*) as shown in Fig. 2. *M_{rs}* is the reset transistor and *M_{rd}* acts as a source follower. *M_x* and *M_y* are the address transistors that perform the serial pixel readout. The serial readout data is then processed by the signal processing circuit. Typical digital control waveforms of the imager are shown in Fig. 2. During the imager operation, there are three periods in a single scan circle: RESET, SAMPLING and HOLD. First, in the RESET period, the signal, *RST* is activated (1.8 V) to charge the emitter terminal of the phototransistor with the impinged optical signals to *V_{dd}* (1.8 V). During SAMPLING period, *RST* is deactivated (0 V) and the signal is sampled through *M_x* and *M_y*. The voltage drop between RESET and SAMPLING period is *V_{arrayout}* which can be calculated according to Eq. (2), where *I_{pt}* is the current generated by the phototransistor when excited by the luminescence, *T_{sample}* is the time of the SAMPLING period, *C_{pt}* is the parasitic capacitance existing in the phototransistor. Finally, in the HOLD period, the signal is processed by the signal processing circuit while the rest of the pixel array is in idle mode. From Fig. 3, the size of each active pixel is 33 μm × 27 μm with a fill factor of 56%. The *W/L* ratios for the transistors in the active pixel are *M_{rs}*

0.5/0.18, M_{Td} 4.8/0.5, M_x 4.8/0.5, M_y 4.8/0.5 (all dimensions are in μm). The size of phototransistor is $20 \mu\text{m} \times 25 \mu\text{m}$. Based on the TSMC 0.18 μm process parameters, the parasitic capacitor C_{pt} can be estimated as 65 fF.

$$\Delta V_{arrayout} = \frac{I_{pt} \cdot T_{sample}}{C_{pt}} \quad (2)$$

All the required digital signals are generated by the on-chip digital circuitry using an external clock source as reference. The analogue data flow is shown in Fig. 2. The pixel array serial output is read out at $V_{arrayout}$ using a CDS circuit [38] followed by an integrator circuit. The basic operation of the circuit in Fig. 2 is as follows: when the signal RST is active (1.8 V), a selected pixel enters its RESET period, the voltage in the sample and hold capacitor (C_{sh}) is clamped at V_{clp} . At the same time the integrator is isolated from the CDS circuit and works as a simple voltage follower. The output voltage of the integrator during the RESET period is V_{clp} , no data will be readout. When the RST signal goes low (0 V), the current pixel enters the SAMPLING period, the pixel array $V_{arrayout}$ output voltage drops proportional to the incident power of the optical signal (i.e., luminescence). Then, C_{sh} samples the drop in voltage and then the voltage is integrated into a DC value by the integrator circuit. Since CDS only samples the voltage drop and the DC level of each pixel is isolated by C_{in} , FPN noise which is caused by pixel mismatch can be greatly suppressed. The output voltage of the CDS block, V_{sh} , can be expressed by Eq. (3). The output voltage V_{out} during the HOLD period can be expressed by Eq. (4). Substituting the value of ΔV_{pixout} obtained from Eq. (4) into Eq. (2), the relationship between V_{out} and I_{pt} can be derived as presented by Eq. (5). Thus, the sensitivity, S , of CMOS imager IC can be calculated using Eq. (6).

$$V_{sh} = V_{clp} = \Delta V_{arrayout} \cdot \frac{C_{in}}{C_{in} + C_{sh}} \quad (3)$$

$$V_{out} = V_{clp} + \Delta V_{arrayout} \cdot \frac{C_{in}}{C_{in} + C_{sh}} \cdot \frac{C_{sh}}{C_{fb}} \quad (4)$$

$$V_{out} = V_{clp} + \frac{C_{in} C_{sh} T_{sample}}{C_{fb} C_{pt} (C_{in} + C_{sh})} \cdot I_{pt} \quad (5)$$

$$S = \frac{\Delta V_{out}}{\Delta I_{pt}} = \frac{C_{in} C_{sh} T_{sample}}{C_{fb} C_{pt} (C_{in} + C_{sh})} \quad (6)$$

The CDS circuit block consists of three (3) switches and two (2) capacitors, and the integrator consists of one switch, one capacitor and an operational amplifier (op-amp). The op-amp used in the integrator is a high-gain high-swing rail-to-rail folded-cascode amplifier [39]. The capacitor values are as follows: $C_{in} = 8 \text{ pF}$, $C_{sh} = 2 \text{ pF}$ and $C_{fb} = 2 \text{ pF}$. With $C_{pt} = 65 \text{ fF}$ and $T_{sample} = 5 \text{ ms}$, the detection sensitivity S can be calculated as 6.12 V/nA (output voltage/generated photocurrent). For a good output dynamic range, V_{clp} has to be set carefully. As seen from Eqs. (3) and (4), V_{clp} can neither be set too high (V_{sh} will get saturated) nor too low (V_{out} will get saturated). The calculated ideal point for V_{clp} is 0.9 V for the current configuration (the ratio of C_{sh} to C_{fb} is 1). Also, considering the dynamic

range of op-amp and mismatch issue of the capacitors, we set V_{clp} at 0.8 V to obtain a good output dynamic range.

Previously, we characterized the performance of CMOS imager IC in terms of responsivity, FPN noise and dark current [8]. A high responsivity for the CMOS imager is important to be functional with weak luminescence signals. We used an orange LED ($\lambda_{peak} = 595$ nm) to illuminate the CMOS imager uniformly. This wavelength was chosen because it is near the peak luminescence from our O₂ responsive luminophore. An external clock generated by a data acquisition system (National Instruments, USB 6218) is used and its frequency is varied from 50 Hz to 1 kHz (equivalent to integration or sampling time, T_{sample} , varying from 10 ms to 500 μ s). Under each sampling time the voltage response of a single pixel is recorded. The LED optical power is measured by a calibrated power meter. Fig. 4 shows the relationship between incident optical power and voltage response under different sampling/exposure times T_{sample} . Detecting weak luminescence signals requires longer integration or sampling times. We selected 5 ms as the sampling time to detect the weak luminescence signals in this work. This sampling time provides a good compromise between achieving high detection sensitivity and acceptable sampling time in this application.

The imager IC die (thickness 380 μ m) was packaged into a custom-designed ultra-thin configuration as shown in Fig. 5(a) (top-view) and (b) (cross-sectional view). A standard microscope cover slip (thickness 190 μ m) was diced into a square of 8 mm $\times$ 8 mm. Gold metal pads 200 nm thick were photolithographically patterned with on the microscope glass slip. The imager IC was glued on top of the microscope cover slip and appropriate connections were wire-bonded as shown in Fig. 5(c). The bond wires were later encapsulated with ultra-violet light curable optical glue (Norland Optical Adhesive NAO60, Thorlabs Inc.) to prevent electrical connection breakage during the sensor integration.

3. Fabrication of xerogel based oxygen sensor materials, PDMS color filters and PDMS trapezoidal lenses

3.1. Xerogel sensor materials

The following reagents were used: tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium(II) chloride ([Ru(dpp)₃]Cl₂) (GFS Chemical Inc.); tetraethoxysilane (TEOS) (Gelest Inc.); *n*-octyltriethoxysilane (C8-TEOS) (Gelest Inc.); hydrochloric acid (HCl) (J.T. Baker); and ethanol (EtOH) (Quantum Chemical Corp.). All reagents were used as received without further purification. Deionized water was prepared to a specific resistivity of at least 18 M Ω -cm using an AmeriWater nanopure system. A sol was prepared by mixing of TEOS (1.448 mL, 6.5 mmol), C8-TEOS (2.052 mL, 6.5 mmol), EtOH (2.52 mL, 44 mmol) and HCl (0.8 mL of 0.1 N HCl, 0.08 mmol). This mixture was capped and magnetically stirred under ambient conditions for 1 h. 25 mM [Ru(dpp)₃]Cl₂ (146.2 mg, 0.3 mmol) in ethanol (5 mL, 85 mmol) was prepared as a stock solution. 0.273 mL of 25 mM [Ru(dpp)₃]Cl₂ in EtOH was pipette into 6.82 mL hydrolyzed sol. This doped sol was mixed on a touch mixer for 1 min. The mixed sol was stored in the dark in the refrigerator. Xerogel based sensor elements were formed from this sol.

3.2. PDMS color filters

The doping of color dyes into PDMS has been previously pursued by other groups [37]. Based on the available literature [37], we selected the Sudan-II dye because its filtering characteristics match with the [Ru(dpp)₃]²⁺ based O₂ sensor with the excitation spectrum centered at 470 nm and emission spectrum centered at 600 nm. Sudan-II (Sigma-Aldrich) is hydrophobic, apolar, and more importantly, incorporates uniformly within PDMS. Stock solution A was prepared consisting of 30 mg/mL Sudan-II dissolved in toluene (anhydrous

99.8%, Sigma–Aldrich). Stock solution B was prepared consisting of 10:1 (v:v) PDMS (Dow Corning, Sylgard 184 silicone elastomer) and curing agent. The Sudan II-doped PDMS solution used to form films consisted of different volumes of stock solution A (from 10 μ L to 35 μ L) in 1400 μ L of solution B. The formulation exhibiting optimal spectral properties for the present sensor was composed of 35 μ L of solution A and 1400 μ L of solution B as shown in Fig. 6(a).

We then characterized the spectral performance of cured PDMS filters of different thicknesses. We kept the Sudan-II dye dopant level as described in the previous paragraph and adjusted the colored filter thickness from 250 μ m to 1000 μ m (Fig. 6(b)). This was done by spin-coating the colored PDMS at different rotation speeds onto standard microscope slides. The PDMS films were cured for 4 h at 65 °C and 30 min at 100°C in a thermal oven. The PDMS films were then left to further cure for 2 days under ambient conditions. This step is crucial to determine if the 470 nm stop-band and 600 nm pass-band are still achieved with lower thicknesses of the PDMS filter. A thinner filter allows the xerogel sensor elements to be closer to the photodetector surface, minimizing dispersion and sensor cross-talk.

3.3. PDMS trapezoidal microlenses

A trapezoidal shape was selected for several reasons: (i) trapezoids have a flat top surface well suited for supporting xerogel thin-films, (ii) trapezoids have wide bottoms providing a rigid and stable structure for contact printing, and, more importantly, (iii) trapezoidal cavities for PDMS casting can be easily fabricated in silicon substrates using tetramethylammonium hydroxide (TMAH) wet etching of $\langle 1\ 0\ 0 \rangle$ orientation silicon wafers [40]. Trapezoidal microlenses were designed with different configurations and spacing to minimize sensor cross-talk while providing a high sensor density and sufficient surface area for xerogel sensor immobilization. The PDMS lenses were fabricated by casting on a microfabricated silicon master. The silicon master fabrication process starts with a 4 inch 381 ± 20 - μ m thick $\langle 1\ 0\ 0 \rangle$ boron doped (conductivity 5–10 ohm-cm) silicon wafer. TMAH was used to etch a silicon wafer. First, a 500 nm of silicon dioxide, serving as masking layer for subsequent TMAH etching, was thermally deposited from pyrogenic steam. Second, a 2 μ m-thick layer of positive photoresist Shipley (S1813) was spin coated and photolithographically patterned through a negative mask to expose squared windows. Third, the oxide over the squares was etched using a common buffered oxide etch solution comprising of a 6:1 volume ratio of 40% NH_4F in water to 49% HF in water. The photoresist was then removed with acetone. Finally, the wafer was soaked in TMAH bath and heated at 85 °C for 144 min to etch trapezoidal cavities (Fig. 7(a)). PDMS was spin-coated to a thickness of 1 mm on the surface of the micro-wells patterned silicon wafer. The PDMS film on the silicon master was cured on a hotplate at 100 °C for 10 min. After curing, the PDMS was cut into 1 cm $\times$ 1 cm pieces containing the micro lenses (Fig. 7(b)).

The ideal solution for a high-density compact sensor array will integrate one photo-pixel with one micro-lens and one sensor element. However, given the weak luminescence signals from the sensor elements (as the surface area of xerogel sensors will be smaller) achieving such a high density sensor array will prove challenging and would probably require long integration times for the imager delaying the complete array read-out or require higher excitation energy resulting in more power consumption. For the current imager, the size of each pixel of the imager is 27 μ m $\times$ 33 μ m. We experimented with PDMS trapezoidal microlenses that had the base area of 1 pixel, 2 $\times$ 2 pixels, 3 $\times$ 3 pixels and 4 $\times$ 4 pixels and different bottom sidewall-to-sidewall spacing combinations of 1, 2 and 3 pixels spacing between the lenses. It is important to note that microlenses of different base areas would have different lens heights as $\langle 1\ 0\ 0 \rangle$ oriented silicon when etched by TMAH has a sidewall angle of 54.74° [40]. We found the ideal configuration with low sensor cross-talk, good

sensor density, and good surface area for xerogel immobilization to be the microlens that covers 3×3 pixels of the imager with 2 pixel spacing between neighboring lenses. Hence, the total thickness of the microlens casted PDMS film is 1 mm plus the height of the lens, which in the present case was $60 \mu\text{m}$ (Fig. 7(c)). Fig. 7(b) shows the casted PDMS trapezoidal lenses with the top lens area of $100 \mu\text{m} \times 100 \mu\text{m}$ with $70 \mu\text{m}$ bottom sidewall-to-sidewall between each trapezoidal structure. The trapezoidal cavity depth in the silicon master was measured using a profilometer as shown Fig. 7(c).

3.4. Contact printing of xerogel sensor on PDMS micro-lens array

The $[\text{Ru}(\text{dpp})_3]^{2+}$ doped sol described in section IIIa was contact printed on PDMS microlens top. Toward this end, $70 \mu\text{L}$ of sol is spin-coated on the surface of a microscope glass cover slip at 400 rpm for 30 s giving the film a thickness of few microns. The PDMS microlens array is placed lens patterned face-down on the sol coated cover slip for a 2 s contact. Care was taken to perform this step within 10 s after spin coating the xerogel film as the sol gels within a few seconds. Finally, the xerogel coated PDMS micro array is cured in the oven for 2 days at 50°C . Thus, xerogel with a thickness of a few microns are printed atop the PDMS trapezoid microlenses as shown in Fig. 8(a). However, given the PDMS flexibility the trapezoid sidewalls are also coated (Fig 8(a)). Fig. 8(b) shows the optical microscope image of the luminescence emission from the xerogel coated PDMS lens arrays with 470 nm LED light excitation and with no optical filter between the sensor and camera. The overall shape of the luminescence is highly reminiscent of the patterns seen previously for substantially larger frustrated cones design [41]. We notice that the luminescence signal is concentrated near the center of the lens top and becomes weaker as we move towards the lens perimeter. At the lens perimeter the luminescence signal is the strongest. The behavior of the luminescence signal distribution across different regions of the lens structure is discussed in the next section.

It is important to note that accumulation of excitation signal and sensor cross-talk is a factor to consider when noticing the stronger signal across the lens perimeter. Accumulation of excitation signal around the lens perimeter occurs due to the nature of functioning of the microlenses [41]. There is a trade-off between sensor cross-talk, high sensor density, and good surface area for xerogel immobilization as was explained in the previous section. This trade-off was taken into consideration in the designing the layout and density of PDMS trapezoidal microlenses. Hence, in the current work we aim to understand the dependence of sensor sensitivity (slope of the Stern–Volmer plots) on the location the sensor data is recorded, that is, with data averaged over the lens top, lens perimeter or sidewalls, and specific locations on the lens structure.

4. Experimental results and discussion

The experimental setup for characterizing the contact CMOS imaging system included a laboratory DC power supply (INSTEK: PST-3202) and a function generator (TABOR: WW2572) which are used to supply the CMOS imager IC and power the blue LED ($\lambda_{\text{peak}} = 470 \text{ nm}$) which is used as excitation source. The CMOS sensor system is placed in a custom-designed test chamber and the O_2 concentration in the test chamber is controlled by a custom built flow-meter, which consisted of a matched pair of air flow controllers connected to O_2 and N_2 gas cylinders.

Fig. 9 presents Stern–Volmer plots for different configurations of PDMS filters and xerogel sensors. From Fig. 9, we characterized the performance of both Sudan-II doped PDMS optical filter film and a configuration where the xerogel was coated on clear PDMS film and combined with a separate Sudan-II doped PDMS film while maintain the same thickness in both the cases. The performance of PDMS films were also compared with that of standard

commercially available acrylic film filters (Edmund Optics, NT39-418, $\lambda_{\text{long-pass}} = 570 \text{ nm}$) coated with xerogel films of the same thickness. The sensors were excited with 470 nm radiation from an LED and a standard silicon photodetector (Thorlabs Inc., PDA 10) was used to monitor the emission response from the sensor materials. In all the cases the Stern–Volmer response was linear and matched the expected responses [6,8,17,22]. We notice that the sensor sensitivity or the slope of the Stern–Volmer response was highest in the case when xerogel was coated on a clear PDMS film and combined with a separate Sudan-II doped PDMS film and its performance was even better than using commercial acrylic film filters. This dual layer structure was used in implementation of the contact CMOS imaging of O_2 sensor array. The xerogel sensor materials were coated over the clear PDMS lens array and combined with Sudan-II doped PDMS film which was carefully aligned and placed on top of the CMOS imager IC.

Fig. 10 shows the image acquired by the CMOS imager IC at 100% N_2 (or 0% O_2) concentration. The imager area allowed a 4×4 array of xerogel sensors to be contact imaged. The CMOS imager IC consumed an average dynamic power of $625 \mu\text{W}$ with 1.8 V DC power supply. As expected, the sensor luminescence intensity decreased as the O_2 concentration increased in the test chamber (as seen from Fig. 11). Inspection of Fig. 10 shows that the emission from the lens top is weaker in comparison to the emission from the lens perimeter as expected from our discussion in the previous section with Fig. 8(b) and previously related work [4141]. Hence, we focused on understanding the obtained sensor sensitivity (Stern–Volmer response) instead of absolute intensity measurements which may include leaked excitation signal.

Fig. 11 shows the Stern–Volmer response using the CMOS imager IC. Here, several data points were taken from near the center of the lens top and from the lens sidewalls (or perimeter). These points were averaged respectively for several photo-pixels and for several experiment runs conducted over a period of 1 week. The imager offset voltage (800 mV) was subtracted from the measured voltage values for the different O_2 concentrations. The obtained data exhibited a linear Stern–Volmer response for both the readings taken from the top of the lens structures and from the lens sidewalls. However, the values taken from the top of the lens structure provided expected performance with good sensitivity and comparable with readings from Fig. 9. However, the values recorded from the sidewalls did not provide the anticipated sensor response. One explanation for this behavior may be due to the fact that the sidewalls of the lens structures seem to collect and focus more of the excitation light which is not effectively filtered by the PDMS filter layer and hence the sidewalls appear brighter. Hence, near the sidewalls the background excitation signal is overpowering the weaker sensor luminescence signal. To resolve some of the ambiguities here, a subsequent study could focus on selectively micro pin-printing *only* on top of microlenses.

Fig. 12 shows the Stern–Volmer responses when recording the voltage values from specific locations on the lens structure instead of considering large regions as shown in Fig. 11. The selected sensor-lens structure provided intermediate sensitivity to avoid skewing the results. We selected four locations specifically, center of the lens top, midpoint between lens center and lens sidewall, midpoint of a lens sidewall, and corner of two sidewalls. The Stern–Volmer response shows expected result for the data considered from the center of the lens top and midpoint of a sidewall as previously seen in Fig. 11. However, it was interesting to notice that the Stern–Volmer response for the data considered at the corner of two sidewalls and midpoint between lens center and lens sidewall showed a sensitivity that is in between for the data considered from the center of the lens top and midpoint of the lens sidewall. Understanding the dynamics of optical signals within the microlens structures may require more modelling, simulations and multispectral imaging and is beyond the scope of the

current experimental work. But the obtained experimental results will provide an important scientific basis such a modelling and simulation work. The concepts, devices, and sensor system demonstrated in the current work will serve as an important step towards the development of compact sensor microarrays.

5. Conclusions

We demonstrate a contact CMOS imaging system which detects luminescence response from a xerogel sensor array for O₂ detection. We described the fabrication of a PDMS optical filters and trapezoidal microlenses for use in miniaturized optical sensors. We optimized several design variables and configurations in this work. First, we optimized the concentration of Sudan-II in PDMS. Second, while keeping the dye concentration constant, we optimized the thickness of the PDMS film to serve as an effective optical filter. Third, the sensor performance was best when xerogel sensor film was coated on a clear PDMS film and was combined with a separate Sudan-II doped PDMS film. Hence, the PDMS lenses were molded from clear PDMS that are coated with xerogels and separately combined with Sudan-II dye doped PDMS film. Finally, trapezoidal lenses with base area of 3×3 pixels of the imager with 2 pixel spacing between neighboring lenses gave the best performance in terms of low sensor cross-talk, good sensor density, and good surface area for xerogel immobilization. We introduced a novel compact packaging method for the CMOS imager with reduced overall sensor system thickness to less than 2 mm. The technologies reported here can be used to develop low cost and intelligent optical sensor microarrays for the detection of various chemical compounds.

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Figure 1.
Block diagram of the contact CMOS imaging sensor system.

Figure 2.
Schematic diagram of the CMOS Imager IC and typical waveform of key digital signals.

Figure 3. Microphotograph of the CMOS imager IC. The inset picture shows a single active pixel sensor.

Figure 4.
Measured relationship between incident power and sampling time T_{sample} .

Figure 5. Photographs of the ultra-thin packaged CMOS imager IC. (a) Top-view. (b) Cross-sectional view. (c) Complete packaged imager IC. A Canadian one cent coin is used as size reference for (a) and (b).

Figure 6.

Performance Sudan-II doped PDMS color filter. (a) Percentage transmission response based on Sudan II-dye concentration. (b) Percentage transmission response based on PDMS filter thickness for a fixed concentration of Sudan II-dye.

Figure 7.

(a) Microfabricated silicon master with base area of $100\ \mu\text{m} \times 100\ \mu\text{m}$ with $70\ \mu\text{m}$ center to center spacing between each trapezoidal structure. (b) Casted PDMS trapezoidal lenses using the silicon master shown in (a). (c) Profile of the trapezoidal cavity in the silicon master measured using a profilometer.

Figure 8.
(a) SEM image of contact printed xerogel thin-films on PDMS trapezoidal microlenses. (b) Microscope view of the luminescence emission from xerogel coated lenses with excitation by a LED.

Figure 9. Stern–Volmer response of O₂ sensitive xerogel thin-films on PDMS color filters and standard acrylic filters.

Figure 10.

Image collected from the CMOS imager IC integrated with PDMS color filter and contact printed xerogel sensors at 0% O₂ concentration at 25 °C.

Figure 11. Stern–Volmer response of the xerogel sensors from the top and sidewalls of trapezoidal lenses.

Figure 12.

Stern–Volmer response of the xerogel sensors from the center of the lens top, midpoint of the lens sidewall, corner of two sidewalls, and midpoint between lens center and lens sidewall.