

A CMOS Gas Sensor Array Platform With Fourier Transform Based Impedance Spectroscopy

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Abstract—A CMOS gas sensor array platform with digital read-out containing 27 sensor pixels and a reference pixel is presented. A signal conditioning circuit at each pixel includes digitally programmable gain stages for sensor signal amplification followed by a second order continuous time delta sigma modulator for digitization. Each sensor pixel can be functionalized with a distinct sensing material that facilitates transduction based on impedance change. Impedance spectrum (up to 10 KHz) of the sensor is obtained off-chip by computing the fast Fourier transform of sensor and reference pixel outputs. The reference pixel also compensates for the phase shift introduced by the signal processing circuits. The chip also contains a temperature sensor with digital readout for ambient temperature measurement. A sensor pixel is functionalized with polycarbazole conducting polymer for sensing volatile organic gases and measurement results are presented. The chip is fabricated in a 0.35 μm CMOS technology and requires a single step post processing for functionalization. It consumes 57 mW from a 3.3 V supply.

Index Terms—CMOS, delta-sigma, FFT, impedance spectroscopy, sensor array.

I. INTRODUCTION

T HE ADVANCES in CMOS technology are now being extensively incorporated into chemical, mechanical and biological sensor systems. Earlier sensor systems used discrete sensing elements which were interfaced to electrical signal processing circuits. These systems are very expensive and power hungry with limited use only in specific applications. On the other hand, integration of sensors with CMOS circuits, significantly reduces the cost, power and size, enabling hand-held portable sensor systems.

In CMOS based gas sensor systems, sensing materials such as conducting polymers and inorganic metal oxides are used for sensing gaseous analytes. These sensor systems find applications in monitoring green house gases, food processing, process control in industries etc. [1]. Conducting polymers (CPs) are particularly attractive materials for sensing gases because of their ability to sense at room temperature [2], [3] and fewer number of post processing steps involved in CMOS integration. Most sensing materials show cross sensitivity to analytes, which can be mitigated by the use of an array of sensors [4]. Pattern recognition and classification techniques can be used with sensor arrays to improve discrimination amongst analytes using a variety of sensing materials. The impedance of the sensing material changes on exposure to an analyte. Impedance spectroscopy (IS) of the sensing material can provide insight into the nature and concentration of the analyte.

IS has been implemented on CMOS chips using frequency response analyzer (FRA) approach [8]–[11]. Here, the sensing material is excited with a sinusoid and the output is multiplied and averaged with in-phase and out-of-phase sinusoids of the same frequency. The averaged outputs give the real and imaginary components of sensor impedance. While, this approach leads to efficient hardware implementation, the impedance extraction process has to be repeated for all frequencies of interest. This makes FRA approach relatively slow and unsuitable for instantaneous impedance measurements of non-stationary sensor-analyte systems. A more efficient way of performing IS is to adopt a fast Fourier transform (FFT) based approach [12], [13], where the sensor is excited with a signal of wide frequency content and the Fourier transform of the output is computed to simultaneously extract the impedance for all frequencies of interest. Although this approach is used in macroscale electrochemistry experiments, it has not been implemented with a chip for gas sensing applications. In this work, we present a sensor array platform in CMOS technology that enables FFT based IS. This paper introduces a CMOS sensor array fabricated in AMS 0.35 μm 4 metal CMOS process. The chip contains 27 sensor pixels which can be functionalized with distinct sensing materials. The front end signal conditioning circuit at each pixel amplifies the sensor signal through digitally programmable gain stages and subsequently digitizes it using a continuous time delta sigma (CT-ΔΣ) modulator. The digital data is read out using a memory addressing approach, for ease of interfacing with an external DSP for off-chip computation of FFT. An on-chip reference pixel is used to extract the phase of the sensor impedance. This pixel also decouples the phase change of the sensor from the phase shift introduced by the signal processing blocks. A proportional to absolute temperature (PTAT) sensor with digital readout is also integrated on chip.
The gas sensing ability of the chip is validated by functionalizing a sensor pixel with a conducting polymer, polycarbazole. Measured results on exposure to acetone and toluene are presented. This paper is organized as follows. Section II details the architecture of the chip. Architecture of each pixel is given in Section III. The need for a reference pixel is detailed in Section IV. Section V describes the design of a PTAT sensor with digital readout. Section VI presents the test setup and measurement results. Section VII concludes this paper.

II. CHIP ARCHITECTURE

The chip contains an array of 27 sensor pixels, a reference pixel and a temperature sensing pixel which are introduced in this paper. The architecture of the chip is shown in Fig. 1.

The bias voltages are generated locally for each pixel to avoid effect of process variations across the chip. A reference current is distributed to all the pixels by a current distribution network. Each pixel accepts an input reference current from the pixel of the same column and previous row and generates the required bias voltages. It mirrors this reference current to a pixel in the next row of the same column. Each pixel can be addressed individually to save the calibration information (described in Section III-E). The addressing is done using NOR based decoders. External address lines \( A_2 \) to \( A_0 \) are used to address the rows while \( A_5 \) to \( A_3 \) are used to address the columns. The digital data from the pixels are read out column wise.

III. SENSOR PIXEL

The sensor pixel contains digitally programmable gain stages (DPGS) for sensor signal amplification. This is followed by a second order CT-\( \Delta \Sigma \) modulator. A calibration cell at each pixel stores the gain settings of the DPGS. The schematic of the sensor pixel is shown in Fig. 2(a). The design of the individual modules of the sensor pixel is detailed in the following sections.

A. Sensor

The electrical impedance of the sensing material changes upon interaction with an analyte. Therefore, it is required to measure the relative change in impedance over its base value to determine the type and concentration of the analyte. This can be conveniently done by using a Wheatstone bridge configuration as shown in Fig. 2(a) [14]. The bridge comprises of four sensor elements \( S_1 \) to \( S_4 \). All the four elements are functionalized with a CP and two opposite arms are passivated (either \( S_1 \) and \( S_3 \) or \( S_2 \) and \( S_4 \)). In the presence of an analyte gas, only the active sensor elements respond and create an imbalance in the bridge.

Interdigitated capacitor (IDC) structures are used to realize each sensor element as shown in Fig. 2(b). The IDCs are designed with Metal 4 (top most metal) of the CMOS process with width and gap of 0.6 \( \mu \)m (minimum dimensions allowed by the CMOS process). PAD layer is defined over these IDCs to etch away the passivation layers [15]. Inset in Fig. 2(b) shows the SEM image of the wells defined by the passivation layer. Post processing steps required for creating wells to confine the sensing material is avoided by this approach. To prevent any damage to the circuits below the IDC structure
during the passivation etching process and to electrically isolate the sensing element from the circuits, a Metal 3 layer is defined below the PAD layer. The cross-section of the CMOS is shown in Fig. 2(c). The bridge is excited with differential signals \( V_{\text{ref}} \) and \( V_{\text{sen}} \) of wide frequency content and the output of the bridge is fed to the underlying signal processing circuits. Reversed biased well-diodes are connected at the input transistors of the first gain stage to prevent gate oxide breakdown during plasma etching of Metal 4. The effect of loading of these diodes is negligible.

B. Sensor Signal Amplification

For a given analyte concentration, the response of the Wheatstone bridge varies with the type of sensing material used. The signal processing circuits following the Wheatstone bridge should account for such variations. The sensor signal amplification is done by digitally programmable gain stages (DPGS).

The need for programmable gain stages can be explained as follows. Consider that a 10-bit ADC is connected in cascade with a DPGS. Let the ADC reference voltage be 1 V, then 1 LSB is close to 1 mV. If the excitation to the Wheatstone bridge shown in Fig. 2(a) is 1 \( \mu \text{V}_{\text{diff,pp}} \), the output voltage of the bridge will be 1 \( \mu \text{V} \) for a 1 ppm response. This signal (1 \( \mu \text{V}_{\text{diff,pp}} \)) should be gain boosted by 1000 to reach at least 1 LSB of the ADC. On the other hand if the bridge response is 100 fV for the same analyte concentration and a different sensing material, \( v_{\text{s'},d} \) will be 100 mV and the sensor signal should be gain boosted by 10 to reach the full scale of the ADC. One approach to achieve this is by cascading three gain stages, of which the first gain stage gives a fixed gain of 10, the second and third stages give gain of either 1 or 10, so that the overall gain of DPGS can be either 10, 100, or 1000.

The circuit schematic of DPGS is shown in Fig. 3. The first gain stage uses a single ended second stage miller compensated opamp with an NMOS input differential pair. The single ended opamp is designed for dc gain of 77 dB and unity gain bandwidth of 10 MHz for load capacitance of 0.5 pF and load resistance of 100 K\( \Omega \). The second and third gain stages of the DPGS are realized using fully differential two stage miller compensated opamps. Each of these stages can be digitally programmed to give voltage gain of either 1 or 10 by switching between the feedback resistors \( R_1 \) or \( R_2 \). Pass transistors are used as switches. All the resistors are realized using the high resistance poly-silicon layer provided by the CMOS process.

C. Opamp Design

The second and third gain stages of DPGS and the loop filter of CT-\( \Delta \Sigma \) modulator (discussed later in Section III-D) use two stage fully differential Miller compensated opamps. The circuit diagram of the opamp is shown in Fig. 4(a) [16]. \( M_1 \) and \( M_2 \) form the input differential pair. \( M_3 \) is biased to carry 20 \( \mu \text{A} \) of current. \( M_5 \) and \( M_7 \) are designed for load capacitance of 2.35 pF and load resistance of 100 K\( \Omega \). Miller compensation capacitor \( C_{\text{C}}, \) of 1.72 pF gives phase margin of 51\( ^\circ \). \( R_{\text{f}} \) of 2.8 K\( \Omega \) cancels the right half plane zero introduced by \( C_{\text{C}}, \). The opamp is designed for unity gain bandwidth of 5.9 MHz and dc gain of 75 dB.

The common mode output of each stage is independently set by two different common mode feedback (CMFB) circuits shown in Fig. 4(b) and Fig. 4(c). The quiescent current through \( M_3 \) and \( M_7 \) is controlled by \( V_{\text{Ref}}, \). Miller compensation capacitor \( C_{\text{CM,1}}, \) of 0.76 pF stabilizes the first stage CMFB loop and gives a phase margin of 61\( ^\circ \). \( R_{\text{CM}}, \) of 9.5 K\( \Omega \) cancels the right half plane zero introduced by \( C_{\text{CM,1}}, \).

A resistor divider based common mode sensing circuit for the second stage of the opamp is shown in Fig. 4(c). We choose \( R_{\text{cmd}}, \) of 1 M\( \Omega \) to reduce differential loading of opamp outputs. \( M_{\text{PC,1}} \) and \( M_{\text{PC,2}} \) form the differential pair of the error amplifier for this CMFB circuit. \( M_{\text{PC,}}, \) is biased to carry 20 \( \mu \text{A} \). Large \( R_{\text{cmd}}, \) leads to instability in CMFB loop and therefore, \( C_{\text{cmd}}, \) of 21 fF is connected in shunt with \( R_{\text{cmd}}, \) to mitigate this issue. Miller compensation capacitor \( C_{\text{CM,2}}, \) of 0.46 pF stabilizes the second stage CMFB loop and \( R_{\text{CM,2}}, \) cancels the right half plane zero introduced by \( C_{\text{CM,2}}, \).

D. Conversion to Digital Data

Multiplexing of the amplified sensor signals for off-chip digitization leads to loss of signal integrity by ambient noise pick up and distortion due to multiplexing switches. To avoid these sources of error, the amplified sensor signal is digitized at each pixel. Among different A/D converter architectures, \( \Delta \Sigma \) modulators are particularly attractive because they provide higher conversion accuracy for lower precision requirements from components and an easier data readout from an array of modulators. Also, the decimation filtering of modulator outputs

\[ \text{Fig. 4. (a) Fully differential two stage opamp. (b) Common mode feedback for first stage. (c) Common mode feedback for second stage.} \]
Fig. 5. (a) DT-\(\Delta\Sigma\) ADC. (b) block diagram of CT-\(\Delta\Sigma\) single bit modulator.

Fig. 6. (a) Second order fully differential low pass CT-\(\Delta\Sigma\) modulator employing CIFF loop filter architecture. The filter is realized using Active-RC integrators. (b) Model of the opamp.

The gain setting of second and third gain stages of DPGS is done using a calibration setup shown in Fig. 2(a). It consists of two latches to store the gain settings. The contents of the latches are controlled by external pins \(CAL\), \(GB_2\), and \(GB_1\). Inputs \(R_i\) and \(C_i\) are row and column select lines from the on-chip address decoder.

IV. FFT BASED IS USING REFERENCE PIXEL

A reference pixel is used to extract the phase change of the impedance of the sensor. This setup also decouples the phase change from the phase shift added by the signal processing blocks. The theory behind use of a reference pixel is introduced in this section using the schematic shown in Fig. 7.

Let the sensor and reference pixel be excited with a signal \(r(t)\) with \(L\) frequency components \(f_1\) to \(f_L\) such that

\[
r(t) = \sum_{l=0}^{L-1} b_l \cos(2\pi f_l t) \tag{1}\]

where \(b_l\) is the amplitude of the sinusoid at \(f_l\). Let \(Z_i\) denote the base impedance of sensors \(S_1\) to \(S_4\) shown in Fig. 2(b) at \(f_1\). Assume that \(S_2\) and \(S_4\) are passivated and do not respond to the analyte. On exposure to the analyte, let the change in impedance of \(S_1\) and \(S_2\) be \(\Delta Z_i\) and \(\Delta \phi_i\). Also let \(Z_i\), \(\Delta Z_i\) and \(\Delta \phi_i\) be the sensor is followed by gain stages, CT-\(\Delta\Sigma\) modulator etc. which collectively add additional phase \(\Psi\) to \(\Delta \phi_i\). \(\Psi\) varies with the frequency of measurement, drifts with time and it is also a function of ambient temperature. Hence it is essential to decouple \(\Psi\) and \(\Delta \phi_i\).

The output of DPGS to the input \(r(t)\) will be

\[
x_s, r(t) = \sum_{l=0}^{L-1} A_{s,f} b_l \cos(2\pi f_l t + \Delta \phi_l + \Psi) \tag{2}\]

Subscripts “s” and “r” denote sensor and reference pixels respectively. \(A_{s,f}\) are the gain settings of the DPGS. In the chip, \(r(t)\) is directly connected to the reference pixel without the Wheatstone bridge. Therefore we can assume, \(|\Delta Z_i/2Z_i| = 1\) and \(\Delta \phi_i = 0\) for the reference pixel. When \(x_{s,r}(t)\) is sampled by the CT-\(\Delta\Sigma\) modulator at \(f_{CLK}\) we get

\[
x_{s,r}[n] = \sum_{l=0}^{L-1} \frac{\Delta Z_i}{2Z_i} A_{s,f} b_l \cos(\omega_i n + \Delta \phi_l + \Psi) \tag{3}\]
where $\omega_1 = 2\pi f_1 / f_{CLK}$. Now, let $v_{n,s} \in \mathbb{N}$ denote the samples of the output sequence from the CT-\(\Delta\Sigma\) modulator due to $x_{s,r} \in \mathbb{N}$ [refer Fig. 5(a)]. Here we use the notation $x[n] \Rightarrow X(z)$ to denote the z-transform for sampling rate of $f_{CLK}$ (640 KHz) i.e.,

$$X(z) = \sum_{n=-\infty}^{\infty} x[n]z^{-n}. \quad (4)$$

Then output of the modulator can be expressed as

$$V_{s,r}(z) = X_{s,r}(z) + NTF(z)E_{s,r}(z). \quad (5)$$

$e[n]$ is the additive quantization noise of the CT-\(\Delta\Sigma\) modulator. We take only N samples of $v_{n,s} \in \mathbb{N}$ for analysis by storing them on a computer after every clock edge. Since $\sum_{n=0}^{N-1} v_{n,s} < \infty$, we can evaluate (5) for $z = e^{j\omega}$ as

$$V_{s,r}(e^{j\omega}) = X_{s,r}(e^{j\omega}) + NTF(e^{j\omega})E_{s,r}(e^{j\omega}) \quad (6)$$

where $\omega$ is the digital frequency in $[0, 2\pi]$. Using (3) and (4) in (6) gives

$$V_{s,r}(e^{j\omega}) = \sum_{n=0}^{N-1} \sum_{l=1}^{L-1} \frac{\Delta Z_l}{2Z_l} A_{s,r} b_l \cos(\omega_l n + \Delta \phi_l + \Psi)e^{-j\omega n} + NTF(e^{j\omega})E_{s,r}(e^{j\omega}). \quad (7)$$

If we sample $V_{s,r}(e^{j\omega})$ for every $\omega = 2\pi k/N$ for $k = 0, 1, 2, \ldots, N-1$ and choose $\omega_1 = 2\pi l/N$ such that $f_l \leq f_{CLK}/200\text{OSR}$ (10 KHz) then, (7) reduces to

$$V_s(e^{j\omega}) = V_s(l) = \frac{N}{2} \frac{\Delta Z_l}{2Z_l} A_{s,r} b_l e^{j(\Psi + \Delta \phi_l)} + e_s(l) \quad (8)$$

$$V_r(e^{j\omega}) = V_r(l) = \frac{N}{2} A_{s,r} b_l e^{j(\Psi)} + e_r(l). \quad (9)$$

$e_s(l), e_r(l) = NTF(e^{j\omega})P_{s,r}(e^{j\omega})$ is the quantization noise of the modulator at $\omega_l$. The reference pixel can be excited with sufficiently large signal to make $A_{s,r} b_l \gg e_r(l)$. Dividing (8) by (9) we have

$$\frac{V_s(l)}{V_r(l)} = \frac{\frac{N}{2} \frac{\Delta Z_l}{2Z_l} A_{s,r} b_l e^{j(\Psi + \Delta \phi_l)} + e_s(l)}{\frac{N}{2} A_{s,r} b_l e^{j(\Psi)} + e_r(l)}. \quad (10)$$

From measurements, the quantization noise power due to $e(l)$ is below $-80$ dB for all frequencies within 10 KHz bandwidth. If the signal power at any given $\omega_l$ is over $-60$ dB then (10) can be approximated as

$$\frac{V_s(l)}{V_r(l)} \approx \frac{\Delta Z_l}{2Z_l} A_{s,r} e^{j(\Delta \phi)} = \Gamma_{s,r} l + j\Gamma_{s,r} l. \quad (11)$$

Equation (11) shows that the real component $\Gamma_{s,r} l$ and the imaginary component $\Gamma_{s,r} l$ of the sensor impedance change can be obtained for every frequency $f_l$ independent of $\Psi$. Decimation of the CT-\(\Delta\Sigma\) modulator outputs reduces the speed requirements of the off-chip DSP while computing FFT. In this work, the FFT is computed on a computer (using Matlab) without performing decimation.

For example, the chip can be clocked at $f_{CLK} = 640$ KHz and the sensor can be excited with a wide band signal containing frequencies from 625 Hz up to 16th harmonic of 10 KHz, and 1024 data samples of reference and sensor pixel can be obtained. Then the ratio of first 16 bins of 1024 point FFT of the sensor and the reference outputs gives the impedance change at these frequencies.

A functionalized sensor pixel is excited with a broadband signal (periodic sinc with 19 frequency components and a square wave) and measurement results of FFT based IS using this approach are presented in Section VI.

To measure the phase desensitization (decoupling of $\Psi$ from $\Delta \phi$), the reference and sensor pixels are excited with $-30$ dBFS (100 mVpp) sinusoid of 3.125 KHz and $A_{s,r}$ is set to 10. The phase of sensor pixel excitation is varied from 0° to 355° in steps of 5°. 8192 point Hann windowed FFT of the modulator output is computed. Further the phase is extracted using the above approach. It is found that the normalized RMS phase error is less than 1.2%. It should be noted here that for small impedance changes, (10) shows that the accuracy of impedance extraction degrades due to quantization noise.

The sensor can be excited with moderately strong voltages to improve SNR and detection limit. The non-linearity of the sensor manifests as harmonics at the output [20]. Harmonics existing within 10 KHz can still be captured by FFT based IS. But this is not possible in FRA based IS where only small signals are used to avoid non-linearity.

V. TEMPERATURE PIXEL

The sensitivity of gas sensing materials is prone to variations in ambient temperature [21]. It is essential to have an on-chip temperature sensor to mitigate the effect of these variations. One pixel of the sensor array is dedicated to measure the temperature. A PTAT based sensing element is used for our design.

Consider two identical diodes $D_1$ and $D_2$ of junction area $A_1$ and $A_2$ respectively. If the diodes are sufficiently forward biased with identical currents then, the difference in the forward bias voltages is given by [22]

$$V_{T_{emp}} = \phi_T \ln \left( \frac{A_2}{A_1} \right) \quad (12)$$

where $T$ is the absolute temperature, $K$ is the Boltzmann constant, and $\phi_T = kT/q$ is the voltage equivalent of temperature.

Equation (12) shows that the voltage difference $V_{T_{emp}}$ is linearly proportional to absolute temperature. $V_{T_{emp}}$ is connected to the input of a pixel by replacing the IDC structure. $I_{bias}$ of 5 $\mu$A is used to forward bias two diodes with $A_2 : A_1 = 8 : 1$. With this approach, the absolute temperature of the chip can be read out digitally.

VI. MEASUREMENTS

The chip is fabricated in Austria Microsystems 0.35 $\mu$m 4 metal CMOS process. The micrograph of the chip is shown in Fig. 8(a).

A. Chip Characterization

The reference pixel and sensor pixels are characterized by manually shorting the opposite arms of the Wheatstone bridge using a micro-manipulator. The pixels are excited with a differential sinusoid of 3.125 KHz and clock of 640 KHz using Agilent 81150A function generator. All the external digital signals
Fig. 8. (a) Micrograph of the chip. (b) Test setup for gas sensing.

\((Gb_0, Gb_1 \text{ and } CAL \text{ and address lines})\) are controlled manually using the setup shown in Fig. 8(b). The chip outputs are logged for 0.5 s using Lecroy MSP-500 mixed signal oscilloscope and later analyzed on a PC.

Fig. 9 shows the power spectral density (PSD) of the pixels for \(-24.3 \text{ dBFS and } 3.125 \text{ KHz input}\). The PSD is obtained by averaging 32 sets of 8 K point Hann windowed FFT of the output of each pixel. It can be seen that the noise shaping closely resembles an ideal \(\Delta \Sigma\) modulator. Degradation of in-band signal to noise ratio (SNR) can be due to non ideal opamps and clock jitter [23]. Distortion peaks present at harmonics of the fundamental are also introduced by gain stages preceding the CT-\(\Delta \Sigma\) modulator. Fig. 10 shows the variation of SNR and signal to distortion noise ratio (SNDR) for gain setting of 10 and 100 across different pixels. Peak SNR of 55.2 dB is obtained for \(-16.4 \text{ dBFS input}\) while Peak SNDR of 49.6 dB occurs at \(-26.8 \text{ dBFS input}\) for gain setting of 10. The measured dynamic range (DR) is 49.6 dB and 48.9 dB for gain setting of 10 and 100 respectively. Table I summarizes the measurement results. Table II compares this work with other CMOS gas sensor architectures. Our chip consumes only 1.9 mW per read out channel. Although the power/channel in [24] is 49.4 mW, the chip performs only dc measurements with limited resistance range. To the authors’ knowledge, no previous work has demonstrated a CMOS gas sensor array platform that enables FFT based impedance spectroscopy.

### B. Gas Sensing

The chip is functionalized with polycarbazole (PCz) to sense volatile organic gasses (VOCs). 1 mg of PCz dissolved in 1 mL of N-methyl-2-pyrrolidone (NMP) is drop coated on all the four IDCs of a sensor pixel and air dried to remove residual solvent.
The volume of each sensor well is only about 60 pL. A sensor well is fully filled while drop coating. The Wheatstone bridge are passivated with polydimethylsiloxane (PDMS) using digital micro-injector. The test setup for exposing the chip to VOCs is shown Fig. 8(b). A small aluminium chamber with a lid is used to confine the analyte gas. Fig. 11 shows the time response for two different concentrations of acetone in ambient environment for 3.125 KHz sinusoid. The inset in Fig. 11 shows the impedance spectrum obtained by exciting the chip with a periodic sinc waveform of 19 tones from 468.75 Hz to 8906.25 Hz and exposing it to 10 K ppm of acetone in ambient. Inset shows the obtained as described in Section IV. The same sensor pixel is exposed to different concentrations of toluene diluted with synthetic air using Kintek 491 MB Gas Standard Generator. The response of the pixel to different concentrations of toluene after baseline correction is shown in Fig. 12 for 3.125 KHz and 400 Hz (18.4 dBFS) sinusoidal excitation. Inset in Fig. 12 shows the obtained when it is exposed to 1000 ppm of Toluene and excited with a square wave of 937.5 Hz. Here, the impedance is extracted up to ninth harmonic.

1) Mechanism of Gas Sensing by Polycarbazole: In CP films, multiple mechanisms such as swelling, de-doping, structural changes contribute towards the change in impedance on exposure to an analyte gas [30], [31]. Most deposition techniques including drop-coating of PCz results in hole dominated conductivity (like a p-type semiconductor) [32]. A redox reaction with a reducing gas like ammonia, will de-dope the polymer and hence the resistance increases. On the other hand, VOCs such as acetone and toluene do not react with a CP at room temperature and the impedance change is mainly due to weak interactions between these analyte molecules and the polymer matrix [33]. From DC-IV measurements, we have observed that the conductivity of PCz decreases on exposure to acetone but increases on exposure to toluene. This is also evident from the change of sign of for acetone (Fig. 11) and toluene (Fig. 12). We have qualitatively discussed the reason for this behavior below.

Acetone is a polar molecule having a dipole moment due to high electronegativity of oxygen atom (shown in Fig. 13). When acetone is absorbed into the PCz matrix, the electric dipole interacts with the delocalized electrons of the polymer backbone and acts as a scattering sight against charge transport. This leads to increase in resistance of PCz. While toluene is a non-polar molecule, absorption of toluene into the PCz matrix leads to swelling of PCz thereby increasing the effective volume for conduction [33].

2) Equivalent Model of a Sensing Element: Here, we have presented an equivalent electrical circuit to model the gas sensing behavior of PCz. Fig. 14(a) schematically shows the
The negative sign arises because sensor elements $S_2$ and $S_4$ (refer Fig. 2(b)) are passivated with PDMS and an increase in resistance of PCz present in sensor elements $S_1$ and $S_2$ inverts the signal fed to DGPS. From measurements we obtained $\Gamma_R \approx 18 \mu \text{ppm/ppm}$ of toluene and $\Gamma_R \approx -7 \mu \text{ppm/ppm}$ of acetone for $A_{sr} = 10$. $\Gamma_R$ of PCz shows frequency dependence on exposure to acetone but not to toluene, this difference can be used to distinguish the two gasses.

### C. Noise Analysis and Detection Limit

The signal band lies within the flicker noise corner of DGPS. From simulations, the worst case SNR achievable at the output of DGPS in 10 KHz bandwidth is 72 dB for gain setting of 1000. The maximum SNR achievable for an ideal second order $\Delta\Sigma$ modulator with NTF described in Section III-D is 51 dB. Therefore the effect of noise at the output of the $\Delta\Sigma$ modulator is dominated by quantization noise.

CPs also contribute flicker noise due to the presence of charge traps in the polymer matrix. The noise contribution also depends on the analyte gas being sensed, absorption and desorption processes, type of polymer etc. Analysis of noise contribution from CP is fairly complex and is beyond the scope of this work.

The lower detection limit of each pixel can be determined from the SNR plots shown in Fig. 10. The minimum signal strength for SNR $> 0$ for gain setting of 10 is $-76.3$ dBFS ($505 \mu \text{V}_{pp}$). From measurements, we obtained $|\Gamma| = |\Delta Z/2Z| \approx 7 \text{ ppm/ppm}$ of acetone and $\approx 18 \text{ ppm/ppm}$ of toluene for gain setting $A_{sr} = 10$. For $1 \mu \text{V}_{pp}$ excitation of the sensor, at least $505 \mu \text{V}_{pp}$ should appear at the input of DGPS for the gas to be detected. This will happen when $\Delta Z/|Z| = 505 \mu \text{ppm}$. Since 1 ppm of acetone causes 14 ppm change in $\Delta Z/|Z|$, we can detect acetone down to 36 ppm. Similarly we can detect up to 14 ppm of toluene. This is a theoretical lower bound. However, in practice, the detection limit is governed by other factors such as stability and flicker noise etc. of CPs.

### D. Comparison of FFT and FRA Approach of IS

Initially, the sensor pixel is exposed to synthetic air and it is excited with a square wave of 937.5 Hz. The impedance is extracted up to ninth harmonic using FFT approach. Further, the sensor is excited with sinusoids of frequency varying from 937.5 Hz to 8437.5 Hz in steps of 1875 Hz and the impedance is extracted using FFT approach. For this particular sensor pixel functionalized with PCz, measurements shown in Fig. 11 and Fig. 12 indicate that impedance change of PCz on exposure to acetone and toluene is predominantly resistive or $\Gamma_I \approx 0$. This is because, each sensing element of the Wheatstone bridge contains only about 60 ng of PCz that spreads out in $192 \times 138 \mu \text{m}^2$ well. The thickness of PCz film is negligible compared to separation between electrodes of the IDC structure (600 nm). Therefore the capacitive component of the sensor element is dominated by $C_{air}$ and changes in $C_{PCz}$ cannot be picked up by $\Gamma_I$. With these considerations, we can simplify the model shown in Fig. 14(b) to an equivalent passive circuit shown in Fig. 14(c). A simple representation for the $R_{eff}$ can be

$$R_{eff} = R_0 \left(1 + \frac{\Delta R}{R_0}\right)$$

where $\Delta R$ accounts for the deviation of the sensor element from a fixed resistance of value $R_0$. It incorporates the change in resistance on exposure to gas, non-linearity at the Al/PCz/Al interface, frequency dependent resistance change, etc.

Using (13) in (11) we can express $\Gamma_R$ as

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$$\Gamma_R = -\frac{\Delta R}{2R_0 \cdot A_s}$$

where $\Delta R$ accounts for the deviation of the sensor element from a fixed resistance of value $R_0$. It incorporates the change in resistance on exposure to gas, non-linearity at the Al/PCz/Al interface, frequency dependent resistance change, etc.

Using (13) in (11) we can express $\Gamma_R$ as

$$\Gamma_R = -\frac{\Delta R}{2R_0 \cdot A_s}$$

where $\Delta R$ accounts for the deviation of the sensor element from a fixed resistance of value $R_0$. It incorporates the change in resistance on exposure to gas, non-linearity at the Al/PCz/Al interface, frequency dependent resistance change, etc.
Here, we demonstrate the use of on-chip temperature sensor while gas sensing. Toluene at 1000 ppm is used as an analyte gas and Eurotherm 2404 temperature controller is used to set the temperature of the analyte gas. The flow rate of synthetic air (diluent gas) for Kintek 491B is kept constant at 500 ml/min. The sensor pixel is exposed with 1 KHz 1 Vpp sine signal. The measurement results are shown in Fig. 16. The sensor is exposed to 1000 ppm of toluene at $t = 30 \text{ min}$ and $t = 55 \text{ min}$ for 5 min when the temperature of the gas is 35°C and 45°C. Fig. 16 shows $\Gamma_{\text{temp}}(t)$ which is the dc value of 1250 point Hann windowed FFT of the temperature pixel. $\Gamma_{\text{Temp}}(t)$ closely matches with the settings of the PID controller. The variations seen at 35°C are due to overshoot of current fed to the heater from the PID controller. The delay in response of the sensor is due to long gas line (about 1.5 m). The response of the sensor at 45°C is 23% higher than at 35°C. Hence, it is important to monitor the ambient temperature to reliably measure the gas concentration.

VII. CONCLUSION

In conclusion, a CMOS sensor array platform with digital readout has been fabricated in 0.35 μm CMOS process. There are 27 sensor pixels and a pixel for temperature sensing. The signal conditioning front-end at each pixel performs sensor signal amplification and digitization using a CT-ΔΣ modulator. Fast Fourier transform based impedance spectroscopy is used to extract the sensor impedance change up to 10 KHz. Resolution of 8 bits (SNDR 49 dB) is achieved across all pixels for the gain setting of 10. A novel on-chip technique is proposed to extract the phase of the sensor impedance. This setup also decouples the phase change of sensor from the phase shift introduced by the signal processing blocks. A sensor pixel is functionalized with polycarbazole and measurement results on exposure to acetone and toluene are presented. An equivalent electrical circuit model is also proposed to explain the change in sensor impedance. The response of the sensor has been characterized by changing the temperature of analyte gas thereby demonstrating the need for an on-chip temperature sensor. The chip consumes 57 mW with 3.3 V supply for 640 KHz clock and it occupies an area of $3.3 \times 3.3 \text{ mm}^2$. This chip is a general platform which can be functionalized with different sensing materials like inorganic metal oxides, polymers etc. for sensing various analytes by impedance spectroscopy.

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