CMOS Gas Sensors

Pavel Komarov

I. INTRODUCTION

The ability to sense diverse volatile organic compounds (VOCs) in air is ubiquitous in biological organisms. For animals a sense of smell confers obvious survival advantages: Smell can help one locate better food, avoid danger, find a suitable mate, communicate, et cetera. Likewise some plants exhibit an olfactory sense that can help them better thrive in their environments, and certainly life at the cellular level is capable of many forms of biochemical signaling. The adaptability and versatility of these systems is truly astonishing.

With computing power ever growing and electronic devices becoming ever more present in all corners of our lives (the hailed "internet of things"), the power of integrated sensing can be immense. Numerous applications of a sense of smell for such small, low-power computers have been proposed: toxic gas monitoring in industrial environments [1], examination of exhaled gases for disease diagnosis [2], detection of biological byproducts of common pests in agriculture, and indoor air-quality monitoring [1]. And certainly the creative uses of this technology extend beyond this list.

Yet for all their potential benefits, sensors that can effectively, reliably detect diverse gases have proved massively, prohibitively complex. The problem is that unlike accelerometer or gyroscope systems— which may be relatively simply constructed, rely purely on physical interactions, and require nothing more than a microcontroller, simple software, and a low-noise, high dynamic-range interface IC to operate —, an electronic nose requires consideration of: (1) chemical interactions that may be relatively slow, (2) active-layer degradation over time, which can cause devices to age poorly, (3) catalytic conditions that may be difficult or energy-expensive to achieve, (4) interface ICs that may have to contend with pulsed, intermittent operation, (5) organization of arrays of complementary devices to sense a variety of different VOCs, (6) inclusion and arrangement of preconcentrators, heaters, long diffusion channels, thermal sensors, humidity sensors, and other auxiliary devices, (7) complex, intelligent software to perform principle component analysis (or similar) on sensor data and interpret results with a machine learner, a learner that will require an immense amount of reliable, relevant, carefully-chosen data for training.

II. SENSOR TYPES

So what is the best way to make VOC sensors a reality? After a representative, though by no means exhaustive literature survey, the answer remains unclear. Different researchers seem to favor different technologies (usually chauvinistically related to their own work), and some approaches are more developed than others, but none is clearly best. Many creative solutions exist, so here I explore some of those I encountered and explain some principles of operation.

A. CHEMIRESISTORS

The device I found most commonly mentioned is the chemiresistor. At its simplest, a chemiresistor consists of a patterned surface coated with some conductive or semiconductive material, a sensing layer, that can somehow 'interact' with a gas in a way that effects its conductivity.

I put 'interact' in single quotes because it is not a well-defined term: Gases can cooperate with materials or surfaces in a number of ways. Thus there are many ways such molecules can interplay with the phenomena responsible for conductivity, such as electron tunneling [3]. Gases have been shown to adsorb reversibly on polar or nonpolar surfaces [4], absorb in to materials [5], donate or accept electrons [3], or truly react and change surface chemistry, a process that may or may not be easily reversible [3].
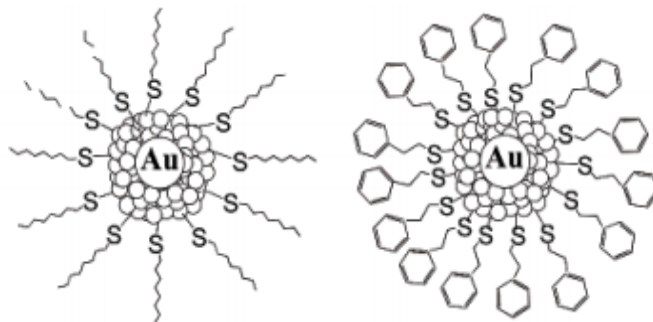

Figure 1 from [6]. Au-thoilate nanoparticles used as the sensing layer for nonpolar VOCs.

Understanding which mechanisms underly

sensing-layer material/gas interactions is important for choosing materials wisely, a critical design parameter. But it is almost impossible to make the sensor perfectly specific. For example, [3] (first figure from [3] shown at right) explores the use of WO_3 nanoparticles to detect H_2S, a highly toxic gas often found as a component of natural gas. The authors express that they do not actually know how the gas interacts with the nanoparticles, but they give a few alternatives and narrow it down to the most likely cause: The gas donates a lone-pair from the sulfur to the oxygen-rich and therefore more-electronegative nanoparticle, raising the Fermi energy of the material. And "[s]ince tungsten oxide is an n-type semiconductor, as the Fermi energy increases, the barrier height for electrons to be excited into the conduction band decreases, and, therefore, the number of thermally excited carriers increases. This causes the resistance of the nanoparticles and therefore the network as a whole to decrease" [3].

Brilliant. But what about other electron-rich gases? Will they not trip the sensor by the same mechanism. Yes, they absolutely will, and from this sensor alone, it may be impossible to tell which gas is causing the resistance-drop. Of course, in an oil refinery the cause is likely to be hydrogen sulfide, but in general it may not be. This underscores one of the most fundamental problems with electronic noses and one of the most common solutions: How can we differentiate between potentially millions of possible compounds? Maybe we do not. Maybe instead we try to solve some other problem with a narrower scope, like keeping refinery workers safe.

But the dream is to not have to obviate the problem, and there is a conception of how to actually solve it [6]: Distinct gases, even those that react by the same mechanism, interact with particular sensing materials in subtly different ways. H_2S reacts best with WO_3 at 300°C; others may react better at other temperatures and will have contrasting concentration-conductivity curves. This is how, by arraying many different sensors, lots of subtle discrepancies may emerge between unmatched gases [6], variations that can together form characteristics identifiable by the right intelligence.
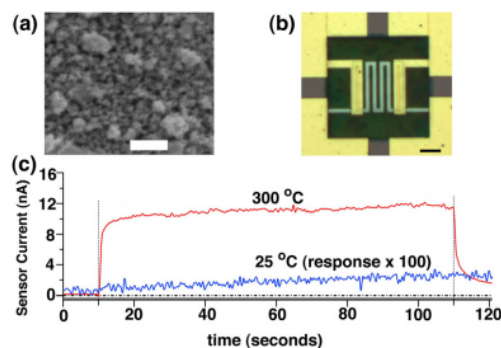

FIG. 1. (a) SEM image of WO3 nanoparticles deposited on a substrate. Scale bar is 500 nm. (b) Optical image of microhotplate. The Pt heating element is suspended on a 500-nm-thick silicon nitride membrane. A 500-nm-thick SiO2 insulating layer separates the gold lead electrodes from the Pt heating element. Scale bar is 100 μm. (c) WO3 nanoparticle sensor current at room temperature (blue, lower) and 300 °C (red, upper) to a 100-s-long exposure.

Chemical reactions are often slow, and many require energy. As a result, depending upon the chemistry, chemiresistors can exhibit almost no activity at low temperature. In the figure above, (c) shows that H_2S and WO_3 interact much more readily at high temperature than at room temperature, necessitating the use of a hot-plate, shown in (b). Hot-plates are, of course, very power-hungry devices, so the authors propose operating the chemiresistor in a pulsed mode. In [7], which is a follow-up by many of the same authors, the group designs a silicon beam suspended over a trench. Optimized for minimal heat dissipation (equal loss to conduction and convection, proved with some elegant calculus) and time-constants on the order of tens of microseconds, the device can be pulsed extremely rapidly, reducing average power consumption from "less than 10mW" to 250μW.
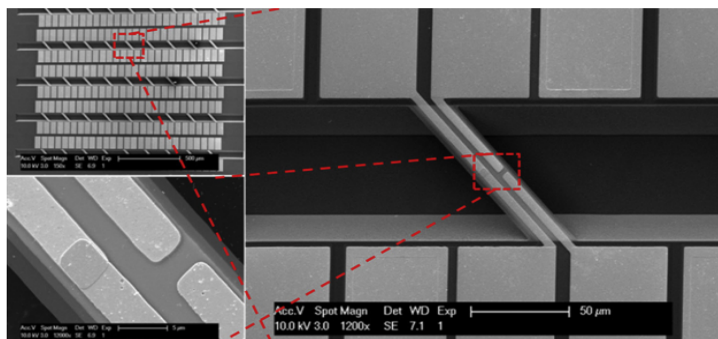

Figure 6 from [7]. "SEM images of the fabricated microheater array. (Upper left) Microheater array showing rows of nine microheaters suspended over trenches. (Right) A single microheater device. (Lower left) Zoom-in on the center of the microheater showing the sensing electrodes with a gap for the sensing layer and a Pt–Au thermocouple junction."

It is relevant to note that the authors of [7] found their device too fast to capture accurate readings above some concentration of H_2S; the chemical interaction responsible for generating a conductivity change is evidently not fast enough to reach full magnitude on super-short time scales. To compensate for this problem, the researchers suggest the device be programmed to operate in extreme-power-saving mode until a rise is detected, then switch to a longer measuring period on each cycle to detect further increases.

It is also worth noting that the authors tested the devices over three months and found the resistance drifted by less than 5% in that time, a variability they consider tolerable for something like a safety sensor, but a shift that could scramble the kinds of subtle queues needed to identify particular gases from sensor array readings. Chemical coatings tend to degrade this way and often have short lifespans, a problem currently the subject of research [1].

B. RESONATORS

Oscillators are excited in to resonance with either rapid heating and cooling, an electric field, or mechanical force, held there with a small input of energy, and observed for frequency shifts due to external stimuli, such as an acceleration or a change in mass. There are many creative ways to build oscillators, including rings [1], disks, cantilevers, and bars, and they have just as many applications.

In [4], the authors employ a sort of modified bar resonator (pictured below) to create a gravimetric sensor. The main body of the resonator is piezoelectrically induced to expand and contract, thrusting the "annexed" platforms inward and outward. These platforms are separated across small connections so the device can resonate without deforming the bulk of either platform significantly, which could "leave the frequency susceptible to equivalent stiffness changes upon sorption of a target."
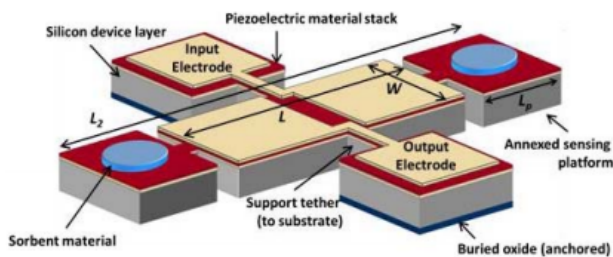

Fig. 1. Schematic diagram of AlN-on-Si gravimetric resonant sensor with annexed platforms.

The resonant frequency of the device is related to its mass by:

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

where k is the stiffness of the resonator and m is its mass. So as gas molecules adsorb to the "sorbent material", typically a nonpolar polymer for detecting VOCs, the frequency will vary as mass varies.

In the end the authors achieve a Q of about 3700 at a resonant frequency of nearly 19 MHz and observe a completely reversible change of -0.09 Hz/ppm for toluene and -0.18 Hz/ppm for xylene.

Unlike chemiresistors, this device does not need to be heated and can therefore operate continuously at very low power. However, this will require some extra intelligence, as frequency shifts unrelated to VOC concentration are possible. For example, the presence of water vapor can cause a negative shift because water sticks to silicon surfaces, and variations in temperature can slightly stiffen or soften silicon, modifying its elastic modulus. To acquire the information necessary to compensate for these factors, a humidity sensor and temperature sensor need to be included.

C. CATALYTIC SENSORS

Reactions of all kinds can be catalyzed in unthinkably many ways, but the most common reaction used for gas sensing is combustion [8]. In [8] Pt nanoparticles and a hot-plate are used to react gases with free oxygen. The reaction follows the Arrhenius equation, so the group provides the following expression:

$$P_{el}(K)=P_{el}(0)-P_{chem}(K)$$

That is, the power required to keep the hot-plate heated to a given temperature is the power it would take were there no chemical reaction minus the power generated from combusting gases. Thus, the quantity of gas present is linearly related to energy usage.
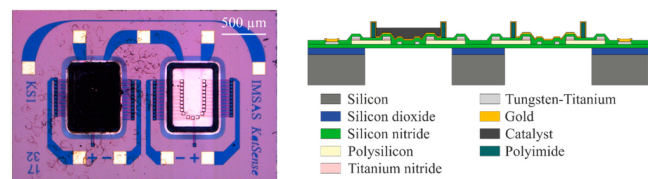

Figure 1 from [8]. " Microscope picture of the sensor (**left**) and a scheme of the sensor structure and materials (**right**)."

Although excellent at detecting gases like hydrogen, this method is not possible for many, more inert gases. And the authors state it "offers low selectivity, only based on [the sensor's] different sensitivities for various gases due to their different heats of reaction." Furthermore, identification of particular gases is impossible: "A gas that causes a low sensor signal at high concentration can be confused with a gas that causes a high sensor signal at low concentration" [8].

D. CAPACITORS

The principle of operation of a capacitive gas sensor is based upon absorption of VOCs in to the dielectric layer [5], which changes its dielectric constant and hence the capacitor's capacitance. As shown in the figure, one of the plates has holes to allow the passage of gas in to and out of the sensing layer.

This arrangement is rare, since one of the plates mostly obscures the sensing layer, causing a possibly-already-slow chemical reaction to be still slower.
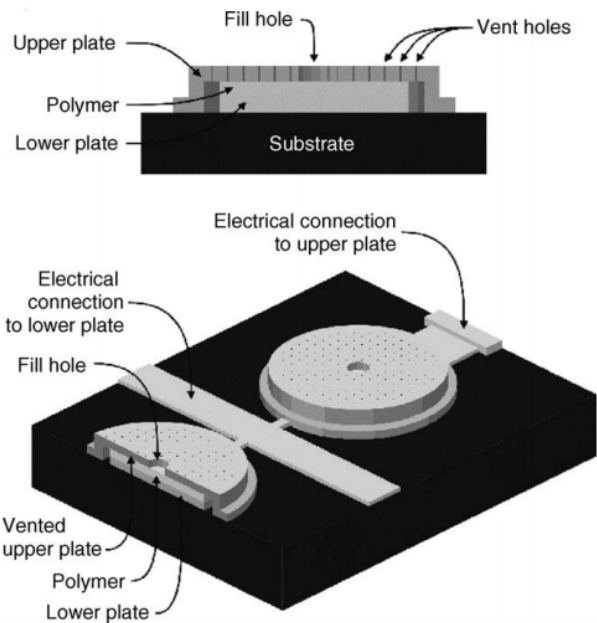

Fig. 2. Cross-sectional diagram of a Seacoast Science parallel plate sensor element.

E. OPTICAL DEVICES

These devices work by observing the refractive index of a sensing layer, which changes as it interacts with a gas [9]. Though MEMs lasers and photosensors are possible and can provide great

precision [10], they are usually not preferred to other technologies which may be simpler, cheaper, and smaller.
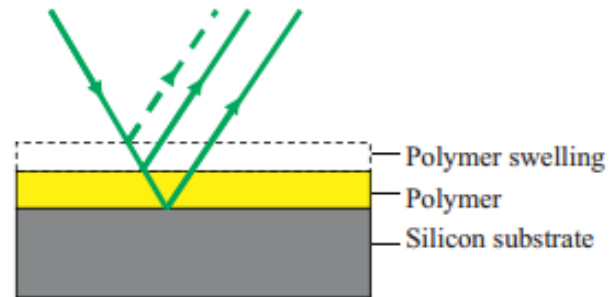

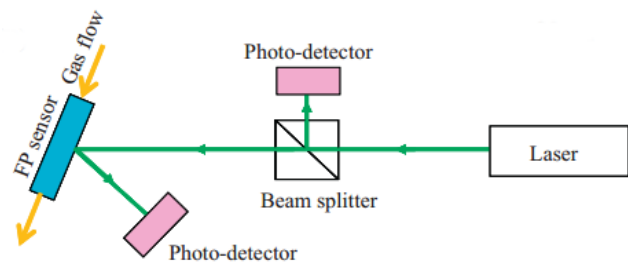**Figure 1** from [9]. "Schematic of the Fabry–Pérot (FP) sensor."

Figure 2 from [9]. "Schematic of the optical detection setup."

III. INTERFACE ICS

Sensors alone are fascinating, but to be useful they must be properly wired. They need to resonate, be amplified, and communicate with unlike sensors or digital computers.

The solution is interface circuits, which is a gigantic field to itself; the possibilities for connecting a device to power, to other sensors, or to a computer are endless. Here I discuss only a few useful interface ICs somewhat related to the sensors shown above.

A. DETECTING RESITANCES

The authors of [11] propose the interface circuit shown in the figure on the next page. Its purpose is to sample the resistance of a gas-sensing chemiresistor that operates in the pulsed mode, that turns quickly on and off and lies dormant most of the time.

It looks complicated, but the paper does an excellent job explaining it. Bias voltages V_{is} and V_{it} are given at the non-inverting inputs of two op-amps. A resistor R_t governs a current out of the inverting
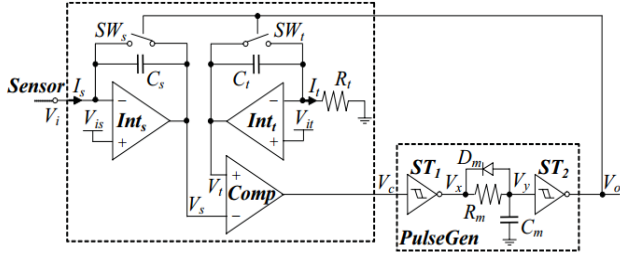
Fig. 3.   Scheme of the proposed interface circuit. The sensor connections are shown in Fig. 1 and Fig. 2.

input of the t-op-amp, which is supplied from the capacitor, causing a voltage decrease on that side and a corresponding increase on the other (blue waveform in figure below).

On the s-side, the opposite happens: a current in charges that side and causes a voltage decrease at the output (green waveform below). When the two voltages meet, the comparator fires a pulse (pink waveform), and the circuit is reset. The PulseGen block (red waveform) can optionally be done in software and is purely to ensure that reset goes to completion.
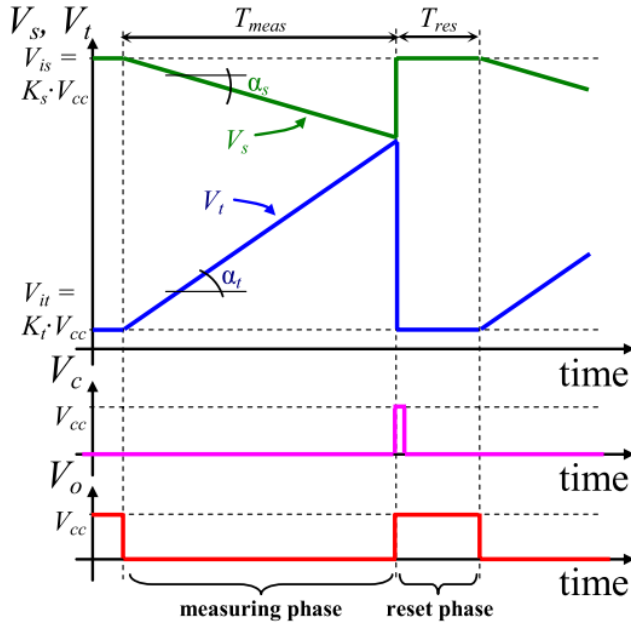

Fig. 4.   Time diagram of the main signals of the circuit in Fig. 3.

The authors then derive an expression for the sensor resistance in terms of the length of time it takes the two waveforms to cross, T_{meas}, and other parameters of their circuit:

$$R_s = \frac{V_{cc} - V_{is}}{C_s \left(\frac{V_{is} - V_{it}}{T_{meas}} - \frac{V_{it}}{R_t \cdot C_t} \right)} = \frac{1 - K_s}{C_s \left(\frac{K_s - K_t}{T_{meas}} - \frac{K_t}{R_t \cdot C_t} \right)}$$

After fabrication and testing, the advantages of this design are shown to be its inexpense, speed, and high dynamic range: "T_{meas} has a five-decade variation (from about 300 ns to about 30 ms, the designed maximum measurement time $T_{meas,MAX}$), whereas the resistance R_s (and current I_s) has a seven-decade variation range, thus showing the time compression effect."

But this interface consumes about 25mW of power, far too much for highly power-constrained applications. The authors of [12] offer a "dual-mode" interface that consumes only "2.6–3.1 µW in the high-R mode and 0.31–2.1 mW in the low-R mode."

The principle for high-R mode (figure below) is to use a voltage-divider to generate a signal and calculate sensor resistance. But if the ratio of the sensor resistance, R_s, to the series resistance, R_L, goes too high, it may not be possible to accurately find R_s for its full range of possible values, as V_{out} will rapidly approach the supply voltage with increasing R_s. So, instead use a programmable potentiometer as R_L with resistance unit-steps size r_u and ensure R_L always matches the sensor resistance to within r_u. If the resistances in question are large enough, then r_u will be small by comparison, and the error of measurements will very small.
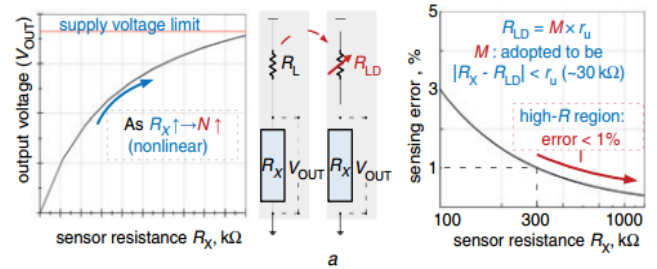
For low-R mode, the authors propose using a programmable current source (figure below), but tuning the supplied current intelligently such that the output can be read with a low-power, 8-bit, successive approximation register ADC.
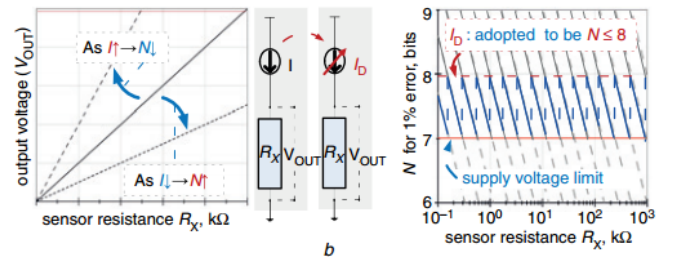
The combined system (pictured on the next page) connects a microcontroller to both systems with switches. Since R_s is constantly tracked, intelligently

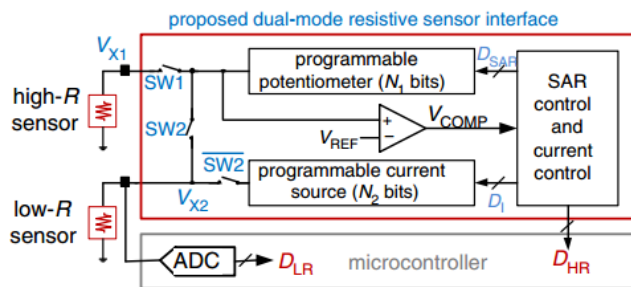switching from one mode to the other is as simple as one conditional statement.

Figure 2 from [12]. "Simplified schematic of proposed dual-mode adaptive sensing circuit"

The group was able to fabricate the device on a 1.8 x 0.8 mm area and demonstrate 1-2% error for a range from 750 Ω to 1.2 MΩ.

B. SUSTAINING RESONANCE

For resonators, the canonical solution is to put them in series with a trans-impedance amplifier (TIA) as depicted in the figure below.
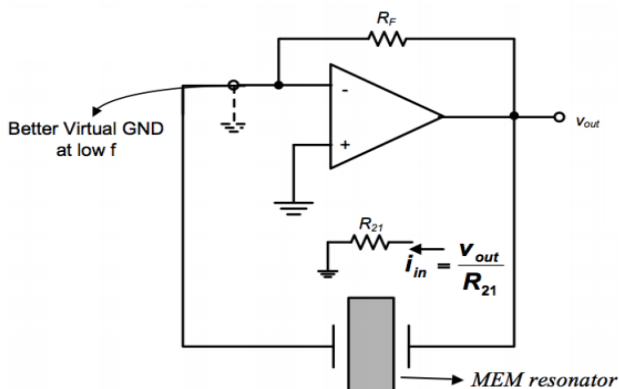

Figure from [13]. Simplification of typical connections between a TIA and MEMs resonator.

In TIA design, it is important to consider phase shifts caused by the resonator itself: In order to induce resonance, the phase shift around the entire loop must be some multiple of 360°. So if a resonator causes a shift, the TIA or adjuvant circuitry must cancel it. Additionally, there may be resonance modes at several frequencies other than the desired fundamental, so the MEMs and interface should be designed to either suppress or avoid them.

For the resonator given in [4], the phase shift from input to output of the MEMs is 0° because the entire device resonates at f_0, and the phase shift at other modes is 180° by design, so they are suppressed

already, and no additional compensation or loading is necessary.

After these critical considerations, the circuit should be optimized for low power consumption and low phase noise. Energy usage can be reduced by choosing a low-power TIA, optimized with multiple stages and no excessively large transistors or currents. The best way to achieve low phase noise is with high Q, as phase noise is inversely proportional to its square as given in the complete phase noise formula below [13]:

$$\mathcal{L}(f_m) = \frac{FkT}{C} \cdot \left[\frac{1}{8Q_{loaded}^2} \cdot \frac{(R_{out} + R_m)}{R_{in}} \cdot \left(\frac{f_o}{f_m} \right)^2 \right]$$

where F is noise figure, k is the Boltzmann constant, T is absolute temperature, C is carrier power, R_m is the resonator's resistance, R_{out} is the output impedance of the amplifier, and f_m is an offset frequency from resonance.

C. CAPACITOR INTERFACE

Despite the rarity of capacitive gas sensors, the interface IC proposed in [5] is simple and elegant and deserves mention.

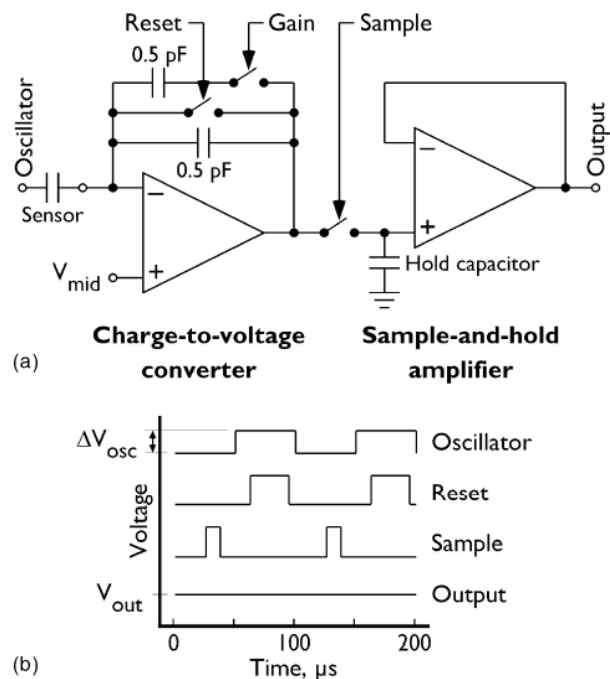
Fig. 7. (a) Diagram of the charge/discharge readout circuit. Opening or closing the "Gain" switch sets the feedback capacitance, $C_{feedback}$, to 0.5 or 1.0 pF, respectively; (b) control and output waveforms for the readout circuit.

Over the measurement period, the sensor develops a charge directly related to its capacitance. Then during sampling the first stage of the interface converts this to a voltage, and the second holds the value for some arbitrary time. The output is related to input by:

$$V_{\text{out}} = V_{\text{mid}} + \Delta V_{\text{osc}} \times \frac{C_{\text{sensor}}}{C_{\text{feedback}}}$$

IV. AUXILLIARY SYSTEMS

One should recognize that none of the sensors explored here operates alone. Already I have listed requirements like temperature and humidity sensors, but there are other requirements too, perhaps less obvious.

What if we need to detect a gas below a sensor's standard range, like gases that are toxic or that indicate health problems in single ppb? The authors of [14], who in 2005 proudly considered themselves to have been the first to assemble a gas chromatograph, make use of a possible solution, a preconcentrator ((b) in the figure below).

Essentially, gas flows in, and VOCs get adsorbed on the surface of carbon nanoparticles. Then at a later phase the entire preconcentrator is heated to shake these molecules off the carbon, and flow is reversed to move them out to the sensor. More advanced versions of this technology, including one based on carbon nanotube "foam" [2] can successfully amplify overall detection by about 10 fold.

What if we need a device to sense multiple gases at once, or we need to detect one gas of many? Because the interactions of multiple gases with sensors can cause a jumble of contradictory information, gases need to be separated prior to . The most common way to do this is with chromatography, a long column filled with some "solid phase" through which smaller molecules are more mobile. In [14] the authors design a spiraled tube for this purpose ((c) in the figure below). At nearly a meter long, the disadvantages of this piece are clear: It is large, and it delays the sensor's reaction time on the order of minutes [14], although faster devices exist [1].

Other auxiliary systems, like a calibration source, are possible. Which to include and how are important design choices.
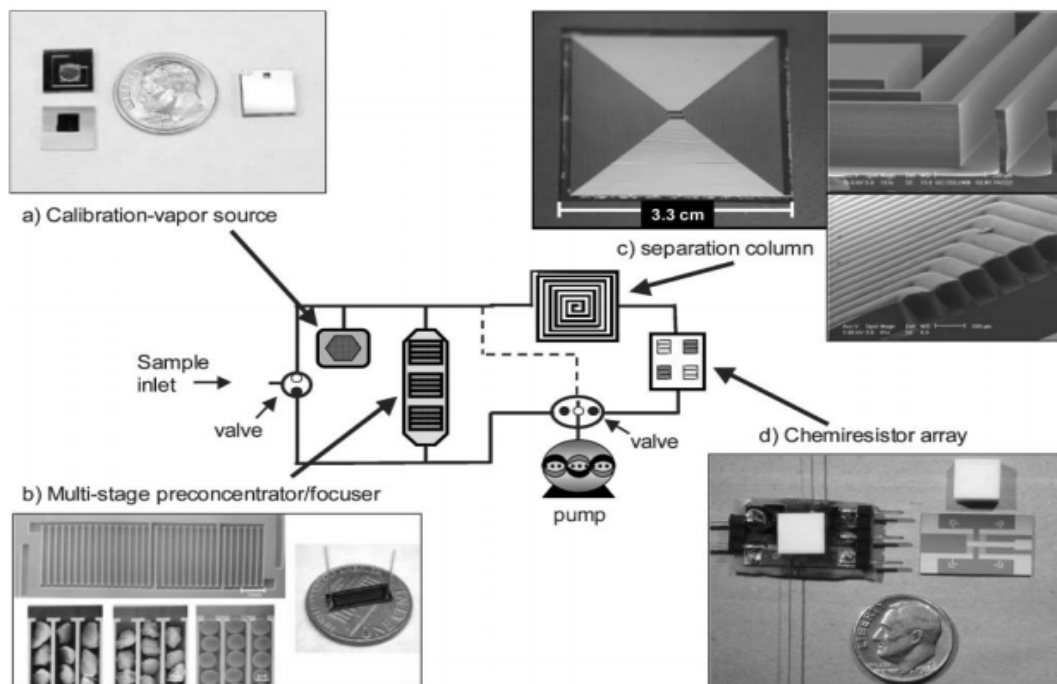

Figure 1 from [14]. "Block diagram of the MEMS mGC prototype analytical system"

V. CONCLUSION

The field is rapidly growing. Fabrication technologies have improved dramatically over the past few decades, and more and more creative gas-sensing technologies are being tried. The most promising are probably high-Q resonators and chemiresistors with specialized, low-power heating systems and fast interfaces.

Additional components like chromatography tubes and preconcentrators are necessary for the most accurate, sensitive results, and these technologies need continuing development [14].

The ability to "smell" lots of compounds at once like biological organisms is not very well replicated with any of these technologies and may require some other sensing concept. Presently, it would be possible to train a machine to recognize various VOCs, but no more than a few at once [14]. And given how much system-specific data would be required for the learning process and how vulnerable current gas sensors are to drift, the effort would likely be fruitless.

Cost remains a barrier for all but the simplest designs, as no others are currently mass produced for sale. As reliability improves, hopefully more designs will pass some threshold of viability and become widely available, making more diverse and difficult usages a reality.

VI. REFERENCES

[1] K. W. Scholten, " Microfabricated Optofluidic Ring Resonators for Sensitive, HighSpeed Detection of Volatile Organic Compounds ", PhD Dissertation, Applied Physics, Univ. Michigan, 2015

[2] J. Lee, et al. (2014) "MEMS Gas Preconcentrator Filled with CNT Foam for Exhaled VOC Gas Detection", DOI 10.1007/s13206-014-9106-y

[3] W. Mickelson (2012) "Low-power, fast, selective nanoparticle-based hydrogen sulfide gas sensor", doi: 10.1063/1.3703761

[4] J. Fu & F. Ayazi (2015) "High-Q AlN-on-Silicon Resonators With Annexed Platforms for Portable Integrated VOC Sensing", Journal of Microelectromechanical Systems, VOL. 24, NO. 2

[5] T. E. Mlsna, et al. (2006) "Chemicapacitive microsensors for chemical warfare agent and toxic industrial chemical detection", doi:10.1016/j.snb.2005.12.066

[6] Q. Cai & E. Zellers (2002) "Dual-Chemiresistor GC Detector Employing Monolayer-Protected Metal Nanocluster Interfaces", Anal. Chem. 2002, 74, 3533-3539

[7] Q. Zhou, et al. (2015) "Fast response integrated MEMS microheaters for ultra low power gas detection", http://dx.doi.org/10.1016/j.sna.2014.12.005

[8] E. Brauns, et al. (2014) "Temperature Modulation of a Catalytic Gas Sensor", doi:10.3390/s141120372

[9] K. Redddy, et al. (2011) "On-chip Fabry–Pérot interferometric sensors for micro-gas chromatography detection", doi:10.1016/j.snb.2011.06.041

[10] A. Q. Liu & X. M. Zhang, (2007) "A review of MEMS external-cavity tunable lasers", doi:10.1088/0960-1317/17/1/R01

[11] A. Depari, et al. (2014) "Fast, Versatile, and Low-Cost Interface Circuit for Electrochemical and Resistive Gas Sensor", IEEE Sensors Journal, VOL. 14, NO. 2

[12] S. Kim, et al. (2014) "Dual-mode wide-range linear CMOS interface circuit for resistive sensors", doi: 10.1049/el.2014.1411

[13] F. Ayazi, (2015) "Basics of MEMS oscillator design using transimpedance amplifiers (TIA)", lecture notes

[14] C. Lu, et al. (2005) "First-generation hybrid MEMS gas chromatograph", DOI: 10.1039/b508596a

[15] D. Zongker, (2000) "Chicken Chicken Chicken: Chicken Chicken", isotropic.org/papers/chicken.pdf