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FINAL PROGRESS REPORT

ADVANCED PERSONAL GAS DETECTORS FOR MINING APPLICATIONS

NIH / NIOSH PHASE I SBIR GRANT #1 R43 OH009026-01
Start date: April 1, 2007. End Date: October 31, 2007.

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TABLE OF CONTENTS

ABSTRACT

Inspite of continuous improvements in hazardous gas monitoring and ventilation, mining remains the second most dangerous occupation in America according to the Bureau of Labor [1]. The risk of explosions in underground mines is high and for workers caught in the vicinity of an explosion, the consequences are frequently catastrophic, as recent disasters in the United States and other countries have demonstrated. The greatest concern is the build-up of hazardous gases (such as combustible gases and carbon monoxide) and reduction of oxygen levels. As a result, in December 2006, a new legislation was put into place [2] that in part requires mine operators to provide an "... MSHA-approved, handheld, multi-gas detector that can measure methane, oxygen and carbon monoxide to *each group* of underground miners and to each person who works alone".

It is recognized that fatalities related to gas explosions and/or fire would likely be prevented or reduced if *all* personnel were equipped with reliable personal gas detectors. However, the size, cost and power consumption of current portable instruments has been a barrier to such deployment. Many end users have suggested that they would be eager to outfit *all* employees (not just the groups or those working alone) with personal protection devices if they were more affordable (currently from $350 for combustible gases, to over $575 for multigas detection). Additionally, the stability, cost and reliability of gas sensors used in such instruments must be improved to enable fail-safe operation. And finally, due to their high power consumption, these sensors require large batteries (often with daily replacement or recharging), further complicating the logistics, increasing operational costs and presenting additional burden to the miner.

Synkera addresses these issues by proposing development and commercialization of a new generation of inexpensive, reliable and portable combustible gas detectors for personal use. This lightweight, credit card sized *Smart Gas Card* is aimed at cost and ease-of-use targets that facilitate use by *all* individuals working in an explosive gas environment. *The Phase I of this SBIR project* was focused on evaluating the feasibility of a critical element of such detector, namely a *low power, high performance reliable microsensor for detection of combustible gases.* This sensor is based on our patented technology that integrates nanostructured sensing elements into a robust monolithic ceramic device and offers numerous advantages relative to existing combustible gas sensors:

- High sensitivity and rapid response time.
- Improved selectivity via advanced operating modes enabled by low thermal mass.
- Superior chemical, thermal and mechanical stability; high reliability and long lifetime.
- Miniature size, low power consumption, flexible design and packaging options.
- Low cost and superior consistency afforded by cost-saving scalable manufacturing.

In the Phase I of this project, Synkera met or exceeded most of the project goals. For the first time, prototypes combustible gas microsensors with power consumption as low as of 50 mW were fabricated and successfully tested for methane detection. A novel "temperature pulse" mode of operation was also demonstrated that increases the discrimination among different combustible gases and reduces power consumption further by as much as 50 to 90%. The Phase I findings clearly demonstrated the feasibility of proposed microsensors and confirmed their potential to enable novel small, lightweight and affordable gas detectors for personal protection in hazardous environments.

The main consequence of the Phase I research is a breakthrough opportunity to develop highly competitive sensors that address the industry needs for low cost and reliable personal gas safety monitors. The proposed sensors and Smart Gas Cards™ have a clear potential to impact mining safety practices by helping mine operators equip every miner with personal multigas detector at a significantly lower cost then with current instruments, thus complying with and exceeding current federal safety regulations. When fully developed and deployed, these products will provide a substantial benefit to worker health and safety and will help to make drastic changes in mining safety, empowering individuals to make life-saving decisions when confronted with hazardous conditions.

This technology also has extremely good prospects in world-wide industrial health and safety markets that are poised to grow substantially as government regulations and industry practices move toward equipping every worker with a complete set of safety tools.

The main objective of the follow-up R&D in Phase II is to advance the microsensor technology to a readiness level that meets required performance targets, to develop and validate the performance of Smart Combustible Gas Card prototypes, and secure partnerships for scale-up and commercialization of combustible gas microsensors and related Smart Gas Card products. Synkera already have commitments from several leading OEM manufacturers of portable and permanent gas safety equipment and are actively pursuing partnership and investment support for launching high volume manufacturing of Smart Gas Cards.

In summary, The Phase I results form a solid framework for a comprehensive Phase II development effort focused on prototyping/demonstration/validation to set the stage for Phase III commercial production of high-performance, durable Smart Gas Card detectors that can significantly improve mining safety, save lives and address significant market needs.

HIGHLIGHTS/SIGNIFICANT FINDINGS.

The following key sensor performance milestones, critical for enabling portable gas monitors and for the Phase I project to be considered a success, were achieved:

- For the first time, catalytic gas sensors with power consumption as low as ~50 mW at 500°C were designed and built, opening the field for development of novel Smart Gas Card personal monitors.
- Novel catalyst compositions and application methods were developed and the resulting sensors demonstrated high sensitivity to methane. Phase I results (40mV with Synkera generic catalyst, 100 mV/% with the catalyst from industrial partner) are close to the originally set target of at least 100mV/%CH_4.
- Evaluation of operating modes resulted in a basic understanding of the advantages of pulsed heater mode for both increasing the discrimination capabilities and enabling long battery lifetime in portable detectors such as Smart Gas Card.

The research conducted in the Phase I also lad the groundwork for developing a comprehensive Phase II development plan and a follow-on commercialization plan. The Phase II project will aim to advance the sensor technology to a readiness level sufficient for incorporation of the sensors in such detectors, and will develop prototype version of the detector.

TRANSLATION OF FINDINGS.

The results of this Phase I project have clearly demonstrated the feasibility of combustible gas microsensors and confirmed their strong competitive advantages of versus conventional sensors, with particularly strong benefits in high sensitivity and selectivity, low power consumption, chemical and mechanical stability and fast response. These features make it possible to develop novel small, lightweight and affordable gas *detectors for personal protection* in mining and other applications where combustible gases could be encountered.

A low power combustible gas microsensor is the missing link that is preventing low cost ($75 with this technology vs. over $350 with current instruments) yet highly reliable and compact personal monitor from being commercially available today. The availability of such instruments, both from a size and a cost standpoint, will lead to a revolutionary new approach to alleviating intrinsic hazards of mining industry by providing every miner with personal safety tools.

OUTCOMES/RELEVANCE/IMPACT.

Combustible gases are an intrinsic hazard in underground mining operations. The proposed miniaturized high performance combustible gas sensors can be used in personal protective devices or permanent instruments to warn users about the presence of this hazard. The sensors have lower power, are more reliable and less expensive than competitive technologies, and will reduce worker exposure and potential health impacts from these very dangerous gases.

These sensors and resulting detectors have a clear potential to impact both mining safety practices and as well as the industrial health and safety market in portable and fixed installations. If successful, it will allow mine operators to comply with and exceed currently updated federal safety regulations by equipping every miner with personal multigas detector at a significantly lower cost.

When fully developed and deployed, these products will provide a substantial benefit to worker health and safety and will help to make drastic changes in mining safety, empowering individuals to make life-saving decisions when confronted with hazardous conditions. This technology also has extremely good prospects in world-wide industrial health and safety markets that are poised to grow substantially as government regulations and industry practices move toward equipping every worker with a complete set of safety tools.

SCIENTIFIC REPORT

INFORMATION CONTAINED IN THIS SCIENTIFIC REPORT IS PROPRIETARY FOR 4 YEARS IN ACCORDANCE WITH FAR 52.227-20

1. PERFORMANCE PERIOD AND KEY PERSONNEL.

This report summarizes the results obtained under NIH SBIR Phase I project "*Advanced Personal Gas Detectors for Mining Applications*", Grant #1 R43 OH009026-01 from April 01, 2007 to October 31, 2007. Synkera currently has 13 full time equivalent employees. The following table lists those who worked on the project during this period.

Personnel	Title	Dates of service	Hours
Dr. Dmitri Routkevitch	Principal Scientist, PI	04/01/07 – 10/31/07	182
Ms. Debra Deininger	Product Manager	04/01/07 – 10/31/07	30
Mr. Clayton Kostelecky	Sr. Project Engineer	04/01/07 – 10/31/07	100
Mr. John Valdez	Process Engineer	04/01/07 – 10/31/07	122
Ms. Erica Benstock	Test Engineer	04/01/07 – 10/31/07	197
Dr. Stephen Williams	President & CTO	04/01/07 – 10/31/07	30
Other personnel	Miscellaneous	04/01/07 – 10/31/07	28
		Total:	**688**

2. BACKGROUND

2.1 The Opportunity: Individual Multigas Portable Safety Monitors

Although continuous improvements in hazardous gas monitoring and ventilation have reduced many of the risks associated with the mining industry, mining remains the second most dangerous occupation in America according to the Bureau of Labor [3]. The mining industry routinely deals with adverse and hard to control natural and environmental conditions. The environmental conditions of greatest concern include the build-up of hazardous gases (such as combustible gases and carbon monoxide) and reduction of oxygen levels. Current gas monitoring is accomplished via both fixed systems and portable instruments. Although it is recognized that fatalities related to gas explosions and/or fire would likely be prevented or reduced if *all* personnel were equipped with reliable personal gas detectors, the size and cost of current portable instruments has been a barrier to such deployment. As a result, in December 2006, new legislation was put into place [4] that in part requires mine

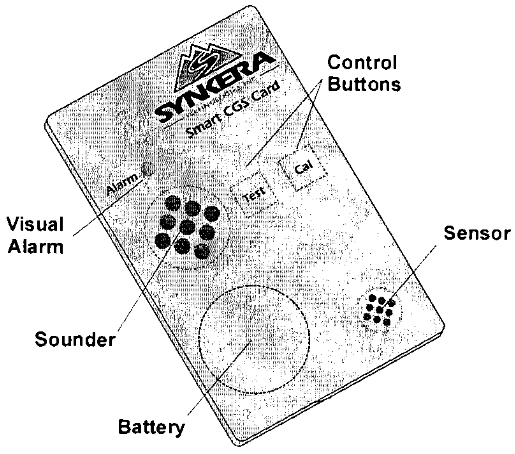

Figure 1. Design concept for proposed Smart Gas Card.

operators to provide an "... MSHA-approved, handheld, multi-gas detector that can measure methane, oxygen and carbon monoxide to each group of underground miners and to each person who works alone, such as pumpers, examiners and outby miners".

In general, the market for personal gas detectors in recent years has been moving towards smaller, cheaper and more sophisticated (usually called "smart") devices. However, mining industry is burdened by the size, cost and performance limitations of existing sensors. Currently, single gas combustible monitors are about the size of a cell phone or larger, mostly due to the large battery volume required to support sensor operation; multi-gas instruments (such as the common 4-gas unit including combustible, O_2, CO and H_2S sensors) are even larger. At the lowest end, single gas combustible monitors retail for \$350 - \$500, while multigas monitors typically cost \$575 and up. Market research performed by Synkera Technologies has shown that there is an opportunity to dramatically expand the market for portable instruments if the cost and size can be substantially reduced. Many end users have suggested that they would be eager to outfit *all employees* (not just the groups or those working alone) with personal protection devices if they were affordable. Also a concern from end users is the amount of "bulk" that each worker is required to carry with them and the likelihood of it being knocked off or otherwise incapacitated, especially in confined spaces. Decreases in detector size and weight will reduce employee objections to carrying or wearing personal monitors.

Synkera has recently developed a new personal monitor concept utilizing a Smart Gas Card format (Figure 1). This is a credit card sized device, designed around a novel line of Synkera low power sensors. The first implementation of this concept is centered around novel solid-state hydrogen sulfide sensors and supporting instrumentation developed under the NIOSH SBIR program [5]. A marketing survey of end users has shown considerable enthusiasm and eager acceptance of this product concept. This opportunity prompted Synkera to prepare a business plan to seek financing for full-scale commercialization of Smart Gas Card monitors. This business plan includes strategies for expanding the Smart Gas Card product line to include low power sensors for hydrogen sulfide, combustible gases, carbon monoxide, and oxygen.

Commercial interest in these products has been extremely high. We see this as the beginning of a safety culture shift towards providing *all* workers, especially in mining and oil and gas industries, with inexpensive and reliable personal gas monitors enabled by a new generation of high performing yet low power sensors, such as the combustible gas microsensor proposed here. Such a device would be ideal for the mining industry, where methane is naturally released during operation creating a risk of underground explosions. In the US, 13 fatalities in 2001, 7 in 2003 and 17 in 2006 (12 in the Sago Mine disaster in West Virginia) were due to explosions from gas build-up [6]. Worldwide, many more miners continue to die annually in gas explosions. Some of the most recent examples of methane and coal dust explosions include Sunjiawan Mine in China (2005, 214 fatalities), Ulyanovskaya Mine in Russia (2007, 108 fatalities) and Zasyadko Mine in Ukraine (2007, over 100 fatalities). Improvements of economic conditions in these countries and growing investments and globalization in the energy and mining sectors will lead to tightening governments oversight and improving industrial practices to improve safety and reduce liabilities, leading to expanding need for personal gas detectors [7].

To summarize, personal Smart Combustible Gas and Multigas Cards, if available, would provide a significant opportunity to improve mining safety and address a very large market. Unfortunately, existing combustible sensors draw too much power to make this type of detector feasible. The ideal combustible gas sensor for such detector needs to be very small, inexpensive to produce, with low power, high sensitivity and high stability. Synkera proposes the development of just such a sensor, based upon our patented micromachined, nanostructured ceramic microsensor platform, and integration of the sensor into a Smart Gas Card detector.

2.2 The Background: Challenges in Miniaturizing Combustible Gas Sensors.*

The sensing of combustible gases is based on the **change in sensor temperature** due to the heat of combustion of gas molecules on a heated sensing element coated with a catalyst ("catalytic bead" or "pellistor", Figure 2). The change in temperature is detected by the resistance of the Pt coil used to heat the bead. This is a fairly mature technology with numerous sensor products available on the market. However, miniaturizing this type of sensor to achieve low power consumption while maintaining performance and reliability has proven not trivial for the industry.

Companies that manufacture combustible gas sensors include those that produce just sensors and those that produce sensors and detection instruments. The two largest companies in the first category are E2V Technologies [8] and City Technology [9], both of whom manufacture a wide array of "bead" type combustible gas sensors. Although both of these companies have sensors marketed for portable applications, their power consumption is in the 220-270 mW range, still too power hungry for truly small portable devices. Though not available for public offering, sensors manufactured by the instrument companies (e.g. MSA, Scott Health and Safety, Detector Electronics) are quite similar to those from E2V and City, with the lowest power at the ~250 mW level. None of these sensors are qualified for the Smart Gas Card detector due to excessive power consumption. We have on-going partnerships with numerous instrument companies, including MSA, Scott Health and Safety, Sperian and Net Safety Monitoring , who are very interested in Synkera's next generation combustible gas sensors with sub-50 mW power consumption.

The closest potential competitor for the proposed sensors is Si-based micromachining technology. Since the late 1980's, Si-based microfabrication have been utilized for the development of gas microsensors fabricated on thin suspended Si_3N_4 or SiC diaphragms equipped with resistive microheaters [10, 11, 12, 13]. These microsensors provide significant advantages with regard to power consumption, precision and uniform temperature control, and rapid response to temperature changes. They also may offer potential for significant price reduction due to intrinsic economies of scale for microfabrication processes. However, implementation of reliable and robust catalytic combustible gas microsensors with this approach remains a significant challenge for a number of reasons.

First, Si-based microsensors have limited utility at temperatures at or above 500°C due to intrinsically *poor reliability* of microheaters deposited on thin diaphragms, while catalytic combustible sensors require 400 to 600°C range. Although some typical refractory materials, such as silicon carbide, silicon nitride and alumina, have been identified as potential substrates [14] for high temperature microdevices, difficulties with their micromachining have prohibited their application in gas sensing.

Second, only limited amount of catalyst can be applied onto the small, flat surface of Si-based microsensors [15], leading to poor sensitivity and easy poisoning. Utilizing lower temperature catalysts has allowed Microsens [16] to developed Si-based combustible gas sensors. However, these devices still requires ~100 mW at 450°C, and feature both the catalytic and the reference elements on the same membrane, leading to parasitic thermal coupling.

Both the current lineup of products from the sensor industry as well as emerging miniaturization trends clearly indicate a strong demand for low power combustible gas microsensors. Intrinsic issues of Si-based microsensor technology have prevented the development of viable combustible gas sensors for ultra-portable personal monitors such as the Smart Gas Card concept.

An affordable and robust combustible gas microsensor technology that can provide low power, high sensitivity, long-term reliability and low cost represents a significant market opportunity by itself. If realized, it could spur a whole new approach to personal gas safety monitoring in mining and other confined space industry applications by enabling Smart Gas Card detectors. Synkera's approach addresses this opportunity by targeting a power level below 50 mW combined with greater performance and reliability at a lower cost.

3. PHASE I SPECIFIC AIMS AND STATUS OF COMPLETION.*

The overall objective of this multi-phase SBIR project is to develop and commercialize a new generation of affordable, reliable and portable hazardous gas detector (Smart Gas Card) for use as a personal safety tool. *The main goal of Phase I was to prove the feasibility of the critical element of such a monitor, namely a low power, high performance reliable microsensor for detection of combustible gases.* The project was successful, and most of the Phase I goals were met or exceeded. The results clearly show that nanoporous alumina can be used as a platform for sub-50 mW combustible gas sensors with high sensitivity, low power and versatile packaging options - all representing significant advantages over conventional catalytic bead sensors.

Specific aims of the Phase I project and status of completion are summarized in the table below.

Specific Aim ***(changes in specific aims initiated during Phase I are highlighted in italic).***	**% Completed**
Based on prior work, select the most appropriate microsensor design(s) for the development of a combustible gas sensor for the Smart Gas Card format. *No changes in Phase I*	100%
Produce and package blank sensor substrates with varied pore diameters, thickness and specific surface area to evaluate their role in sensor performance. *Change: number of variables was reduced to accommodate a higher priority task of developing prototypes for evaluation at MSA.*	90%
Develop methods for catalyst deposition and evaluate several catalyst formulations. Develop a roadmap for Phase II catalyst development. *No changes in Phase I*	100%
Develop and evaluate sensor operating modes, including temperature pulse and modulation.	100%
Thoroughly evaluate the effect of sensor substrate parameters, catalyst formulation and operating mode on the performance of sensors. Identify the most critical factors on sensor performance and stability and provide feedback for sensor development in Phase I and II. *No changes in Phase I*	100%
Produce prototype low power sensors for in-house testing and for independent evaluation by our partners. Demonstrate the potential of achieving performance suitable for portable monitors. *No changes in Phase I*	100%
Finalize application and sensor performance requirements for full scale development of "smart card" monitors. *No changes in Phase I*	100%

The following section summarizes the Phase I results and sets the foundation for technology and product development during Phase II and beyond.

4. PHASE I RESULTS AND DISCUSSION*

4.1 Review of the approach.*

The proposed approach (Figure 2) is based on the unique properties of nanoporous self-organized Anodic Aluminum Oxide (AAO, Figure 3) and Synkera's capabilities in nano- and microfabrication with this material. AAO is an excellent platform for gas sensing, including catalytic combustion type (Figure 2), and represents a paradigm shift in microsensor development and manufacturing. Synkera holds a key patent [17] on using this technology platform for gas sensors and other devices.

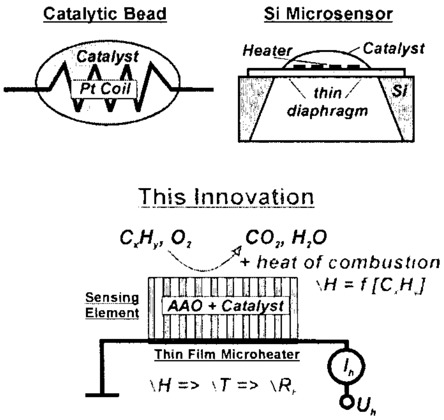

Figure 2. The Innovation

Figure 4 schematically outlines the sequence of sensor fabrication. The nanoporous architecture and ultra-high surface area of AAO provide an ideal host for a well-dispersed and active catalyst, allowing uniform interaction of gas molecules with the catalyst dispersed though the sensing element, and thereby enabling high sensitivity. Additionally, AAO micromachining enables fabrication of thermally isolated monolithic microsensors with superior chemical, thermal and mechanical reliability. Temperature control is provided by a low power thin film microheater, which is deposited on one face of the sensing element and also serves as an integral resistive element temperature detector. The sensing element is heated to a temperature at which it can catalyze oxidation of combustible gases:

$$C_xH_y,\ O_2 \rightarrow CO_2,\ H_2O + \Delta H;\quad \Delta H = f[C_xH_y] \sim \Delta T_{sens} \sim \Delta R_{heat}$$

The heat (ΔH) generated during combustion increases the sensor temperature as a function of the gas concentration, and the change in temperature is detected by the change in microheater resistance, thus providing usable measure of gas concentration. We have outlined below some of the critical elements of the innovation.

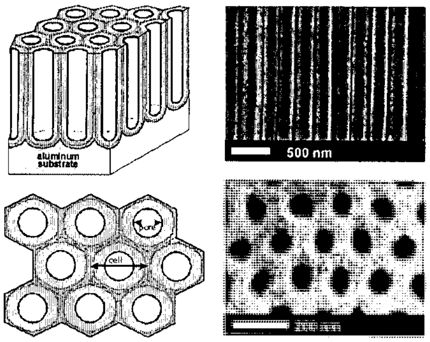

Figure 3. An "artist concept" and typical SEM images of AAO.

Nanoscale Engineering of AAO Morphology. AAO, produced from aluminum foil via an electrochemical process, is an anisotropic material with a high density of uniform and parallel nanopores (Figure 3). AAO pore diameter (5-300 nm), pore density (10^9-10^{11} cm^{-2}) and thickness (1-300 μm) are variable within wide ranges by controlling the conditions of anodization [18, 19]. In this Phase I project, the AAO morphology was fine-tuned in two steps. First, the *"primary porosity"* is defined during anodization. Second, *"secondary porosity"* is formed inside the primary pore walls as a result of annealing of initially amorphous AAO into high surface area (80 m^2/g) polycrystalline alumina (see Figure 4). *This approach yields sensing elements with a 10,000 fold increase in surface area relative to non-porous ceramic.*

Forming Ceramic Microsensors. This project relies on Synkera's Ceramic MEMS technology based on AAO ([20, 21]) for creating low power microsensor substrates. To the best of our knowledge, there is no other ceramic micromachining technique with the same degree of versatility and manufacturability. Anisotropic etching of AAO enables high-resolution bulk-like micromachining and was used in Phase I for making 50 μm wide sensing elements with a power draw of ~50 mW at 500°C.

Deposition of Catalyst. Deposition of catalysts inside the pores and onto the surface of AAO enables catalytic oxidation of combustible gases at the sensing element. In Phase I work, generic Pd/Pt catalysts were used and some metal oxide promoters [22], such as colloidal alumina, were shown to increase catalyst performance. Wet chemistry methods were proven to work well for deposition in very high aspect ratio (length/diameter) pores, yielding good sensor performance.

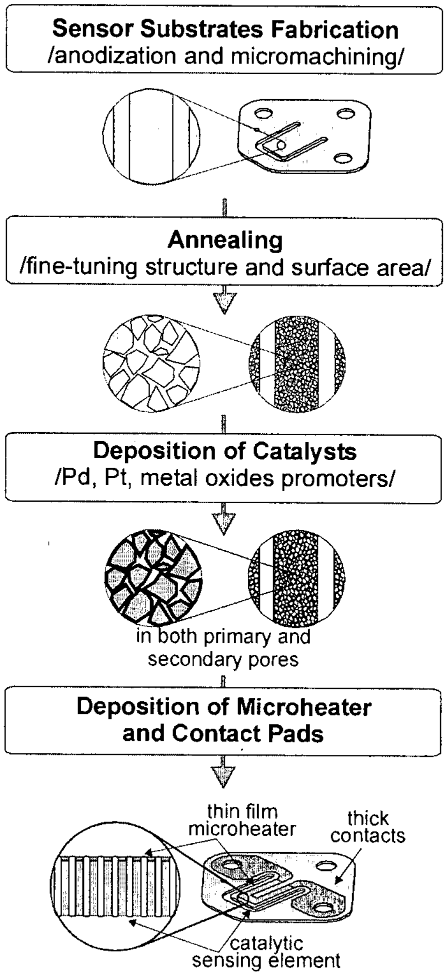

Figure 4. Sensor fabrication sequence.

Advanced Operating Modes. Different gases have different mechanisms and kinetics of combustion. Sensitivity of combustible gas sensors to different gases is therefore a strong function of not only the temperature but also the rate of temperature change. Recently an adsorption/combustion mechanism realized on a microsensor with Pd/alumina catalyst in a heating pulse mode was reported to enable discrimination between different alcohols, including isomers [23, 24]. *The low thermal mass and high sorption capacity of our nanostructured sensing elements are especially amenable to implementing such approaches and create additional opportunities to improve performance.* Using such advanced operating modes as temperature pulse and temperature modulation, in Phase I we were able to discriminate between different combustible gases.

4.2 Initial Sensor Design.*

The main goal of this task was to define the design of low power combustible gas microsensors suitable for Smart Gas Card portable monitors.

There are conflicting aspects to consider in the design of catalytic microsensors for portable monitors:

- Low Power: requires minimizing thermal mass and reducing overall heat losses.
- High Response: requires maximizing the amount of the catalyst per sensing element (specific catalyst volume) and minimizing heat transfer to the reference heater and overall heat losses.
- Manufacturability and Reliability: some features, such as small cross-section of microheater, may negatively impact yield and manufacturability as well as mechanical and thermal reliability.

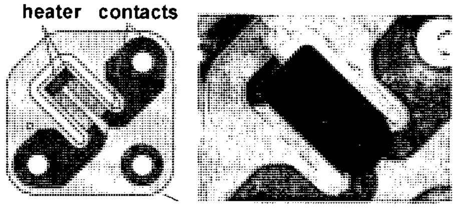

Figure 5. Design outline and image of generic single-element catalytic sensor used in initial development.

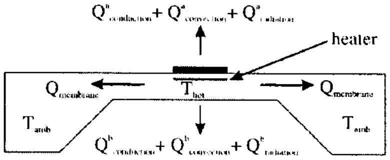

Figure 6. Heat loss mechanisms in microheaters (from [25]).

Although the Phase I design work was primarily driven by the first two aspects, yield and reliability were evaluated as well. In Phase I work we used two types of sensor designs:

1. Generic Single-Element Design from Prior Work.

The generic design (Figure 5) was used in the initial investigation of the role of AAO parameters in sensor performance and in for catalyst development. Although relatively high power (~400mV @ 500°C), this sensor is very reliable and has a large sensing element, which simplified catalyst deposition.

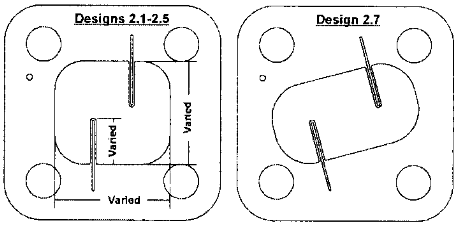

Figure 7. Two our of seven low power designs evaluated in Phase I.

2. New Low Power 2-Element Designs.

This design has two sensing elements (one with catalyst, the other blank reference, Figure 7) used in a bridge circuit to provide compensation for the changes in ambient temperature and drift in microheater resistance. The "U-shape" (with the heated tip) of the sensing elements allowed simplified fabrication and acceptable reliability. The width and the thickness of each arm of the "U" was fixed at 50 μm to achieve the targeted power consumption of 50 mW @ 500°C.

Heat loss for microheaters [25, 26, 27] occurs via the following routes (Figure 6):

- conduction through air: $Q^a_{cond} = G_{air} \lambda_{air} (T_h - T_{air})$ $G_{air} \approx 4 \pi r$
- conduction through support: $Q^s_{cond} = G_s \lambda_s (T_h - T_s)$; $G_s = 4 A / l$
- convection: <5% [28]) due to small size and negligible air flow inside packaging;
- radiation. $Q_{rad} = G_{rad} \sigma \varepsilon (T^4_h - T^4_{amb})$, insignificant (<2-3%) at 500°C;

where Q is heat loss, G is geometrical factor, λ is thermal conductivity, r is heated size, A and l are support beam cross-section and length, σ is emissivity and ε is Stephan-Boltzman constant. Preliminary analysis based on the above equations and selected literature [25, 26, 27] indicated that predominant mechanisms of the heat loss at 500 °C is conduction through air and support.

Even though a quantitative determination of the power consumption cannot be done by simple addition of the different heat losses (numerical modeling is needed for accurate predictions), based on this analysis, the reduction of power should be guided by the following principles: the shape of the heated element should be close to spherical to minimize its area and thus conduction through air, while its mass is not as significant of a factor; the support beams should have low cross-section and high length; the opening in the sensor dies should be maximized. Using these guidelines, the following design options were evaluated in order to (1) identify the opportunities for reducing the power while maintaining high catalytic volume, and (2) evaluate the effect of design on yield and robustness:

- the length of the cold and heated part of sensing elements (increased heated length = greater catalytic volume);
- the distance between the sensing element and the reference (to reduce heat coupling); and
- the size of the open area (to reduce heat loss).

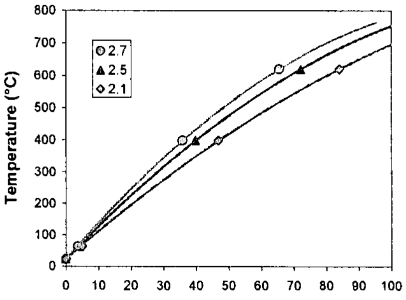

Figure 8. Temperature vs. power for selected designs.

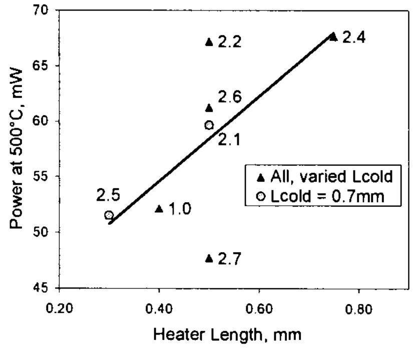

Figure 9. Power vs. heater size for Phase I designs.

Seven new sensor designs were designed, fabricated and evaluated (Figure 7, Table 1). Temperature calibration (Figure 8) was performed applying a small amount of material with known melting point (beeswax (63°C), K_2CrO4 (398°C)) onto a heater as well as visual onset of red glow (620°C). The heater resistance (varied from 12 to 26 Ohm) and power (45-70 mW @ 500°C) were evaluated as a function of design (Table 1). We confirmed that the heater length was one of the main factors in the power consumption (Figure 9), while depositing additional material onto the heater had practically no effect (see section 4.4). This finding provided a clear direction for comprehensive Phase II design optimization effort.

The designs for catalyst deposition and performance evaluation were selected based on the power consumption and yield after fabrication and annealing (designs 2.1, 2.5 and 2.7).

Table 1. Main parameters of Phase I design screening effort.

Design ID	1.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7
Description	prior work	max opening, medium heater	2.1 + shorter cold, smaller opening	2.1 + longer heater	2.2 + longer heater, shorter cold	2.1 + shorter heater	2.1 + offset for wider opening	rotated for greatest separation
Lh, mm	0.4	**0.5**	0.5	0.75	0.75	**0.3**	0.5	**0.5**
Lc, mm	0.2	0.7	0.35	0.7	0.35	0.7	0.7	0.62
H-to-H, mm	0.5	1.04	1.04	1	1	1.22	1.04	**1.8**
Fabrication Yield	medium	high (>80%)	medium	medium	high (100%)	**high (100%)**	medium	high (100%)
Annealing Yield	poor	medium	high	very poor	poor	**high**	poor	poor
Power @ 500°C, mW (±3 mW)	52	**60**	67	-	68	**52**	61	**48**

4.3 Sensor Substrate Fabrication*

The goal of this task was (1) to fabricate generic sensor substrates (for catalyst screening and evaluation of the AAO parameters on sensor performance); (2) to develop a process and fabricate new low power sensor designs for feasibility demonstration.

Blank sensor dies were fabricated as described in section 4.1 and Figure 4 of this report and annealed as needed. Microheaters and contact electrodes were formed by plasma sputtering of Pt (300 nm for the heater, 600 nm for the contacts) through shadow masks. The resulting sensors were annealed at 650°C to condition the heater and packaged onto TO-style 4-pin headers (Figure 12).

Generic Single-Element Sensor Substrates (Figure 5).

1. *Sensors for catalyst screening.* Based on prior work, we produced sensor substrates with AAO parameters most often used at Synkera in gas sensor work: pore diameter 35 nm, thickness 50 µm, annealing to high surface area gamma-alumina. The results are described in section 4.4.
2. *Sensors with varied AAO parameters.* The main goal of this effort was to identify the most significant AAO parameters affecting catalytic uptake and sensor performance to set the stage for AAO optimization in Phase II. The same catalyst formulation (one of the best identified during catalyst screening) was used throughout this work.
   - *Pore diameter.* Limited evaluation of the *pore diameters and the anodization electrolyte* (20 nm, 35 nm and 56 nm, sulfuric and oxalic acid) did not reveal a significant impact on sensor performance. The effect of broader pore diameter (10 nm to 150 nm) and pore density range will be more thoroughly investigated during the Phase II sensor optimization.
   - *Thickness.* We initially planned to evaluate the effect of AAO thickness on sensor power consumption and performance using the large single element sensor. However, after performing the design analysis, it became apparent that the contribution of the thickness will be very design-specific and should be studied only after the low power design evaluation is concluded and recommendations for a preferred design are available (see section 4.1).
   - *Annealing.* Sensor substrates with fixed pore diameter (35 nm) and thickness (50 µm) were produced and used for investigating the effect of annealing on catalyst loading and performance. Annealing affects the specific surface area, phase composition and surface chemistry of AAO and was expected to be one of the main factors in achieving high sensitivity.

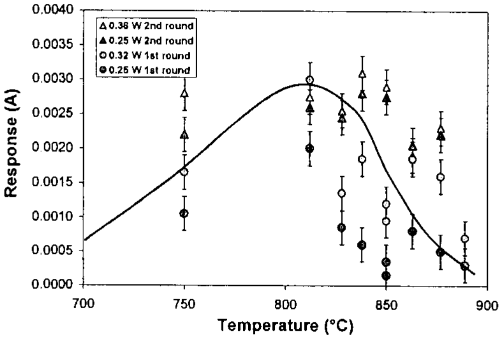

Figure 10. Effect of annealing temperature on the sensor response at to 2.5% CH4 at different power.

Sensor substrates were annealed from 750 to 900°C, to cover the expected phase transformations:

- low surface area (2-3 m2/g) amorphous boehmite phase present from ambient to 750°C;
- high surface area (60-80 m^2/g) polycrystalline γ-alumina formed in the narrow range of 820-880°C;
- decrease in surface area (6-10 m^2/g) due to grain growth in γ- and forming of θ-alumina (~900°C)

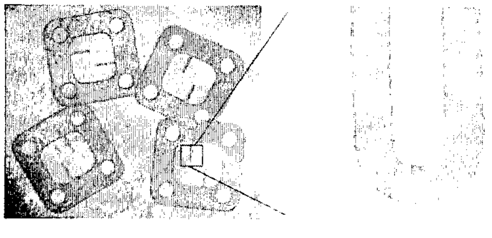

Figure 11. Blank low power microsensor substrates

An equivalent amount of catalyst precursor was applied to each sensor and the response to 2.5% methane as a function of heater power was tested. Although the results (Figure 10) seem to indicate that a greater response was obtained with sensors annealed to 800-850°C, the trend was smaller then expected. Possible reasons may be that the non-optimized Phase I catalyst was not amenable to high surface area support; or that annealing conditions were not optimal for producing high surface area γ-alumina. Phase II will follow-up on this experiment by (1) conducting through BET measurements of AAO surface area as a function of annealing, and (2) re-evaluating the effect of annealing with *low power* sensors and *optimized* catalysts.

Low Power Dual-Element Sensor Substrates.

Fabrication of low power design sensors (Figure 12) was performed in three rounds:

1. *Micromachining process optimization.* Substrates representing all eight low power designs (1 old and 7 new) were produced using the anisotropic etching route. Initial experiments revealed that use of standard conditions resulted in unacceptable (by over 10 µm) over-etch of the microheater structure. Subsequently, the AAO etch conditions (time and temperature) were altered to minimize these problems. This effort was successful and the representative sensors are shown in Figure 11.
2. *Fabricating sensors for design evaluation (yield and power consumption).* Using optimized micromachining conditions, a second round of low power sensors was produced to support the design evaluation described in section 4.1. It is important to note here that even small variations of the sensor design parameters (length, size of the open area) significantly affected the yield after sensor fabrication and annealing as shown in Table 1. Two conclusions are important for the Phase II sensor development: (1) very long microheater arms tended to break during fabrication; (2) stress-relief needs to be introduced to eliminate failure in some designs during annealing.
3. *Prototype fabrication.* Two designs with an acceptable combination of low power and yield (2.1 and 2.5) were selected for further work on fabricating low power sensor prototypes for feasibility demonstration and performance evaluation. A third fabrication round produced over 100 sensor substrates. ***Of these, 50 dual-element sensor substrates were purchased by MSA for evaluation with their proprietary catalyst (see section 4.4). This sale to one of the gas detection industry leaders is a strong vote of confidence in the technology.***

Due to additional time required for process optimization, the early success in demonstrating 50 mW sensors with standard AAO, and the high priority of the MSA prototype fabrication task, the study of the effect of AAO thickness was postponed and will be performed early during the Phase II.

4.4 Catalyst Development.*

The main goal of this task was to identify catalyst formulations that support the development of functional low power prototypes and to outline a path for Phase II catalyst development.

Catalyst formulations (aqueous and alcohol solutions of Pd and Pt nitrates and acetates) were selected based on our prior work and published literature. Metal oxide promoters were deposited from similar solutions or from nanopowder dispersions. Additional variables included Pd and Pt concentration and catalyst loading. The procedure involved manual application (under microscope) of the solution to the sensor, followed by an increase of microheater temperature to ~600°C. *The main criteria* for identifying the most promising catalyst formulation for Phase I feasibility demonstration were: magnitude of response to methane; number of applications needed to maximize the response; and sensor reproducibility. Conclusions from this work are: (1) aqueous solutions of Pd salts provided the greatest response; (2) alcohol solutions, although penetrating well into the pores, did not provide a good response due to low solubility of Pd salts used; (3) Pt deactivated Pd catalyst; (4) deposition of MgO and SnO_2 promoters prior did not increase response; (5) deposition of Al_2O_3 from nanopowder dispersion significantly increased the response by increasing catalytic volume and did not increase the power consumption, (5) the most promising catalyst was a saturated solution of $Pd(NO_3)_3$ in dilute nitric acid. This precursor was stable, provided uniform Pd loading in just 3 to 5 applications, and yielded the greatest response in large sensors. This composition (with and without Al_2O_3 promoter) was chosen for further work on evaluation of the effect of AAO parameters (see section 4.3) and for low power prototype development.

Low power sensors were evaluated with both Synkera catalysts and proprietary MSA catalysts.

- *Synkera catalyst.* Catalyst without Al_2O_3 promoter did not perform well, resulting in very low (7-10 mV/2.5% CH4) signal, and indicated a need for further development in Phase II. However, with Al_2O_3 nanopowder, which formed a nice pellet at the tip of the microheater, the response was as high as 100mV per 2.5% CH_4 (Figure 13).
- *MSA catalysts.* Several proprietary MSA catalysts were evaluated at Synkera and at MSA. The response to 2.5% CH_4 ranged from 70 mV to 250 mV, depending on the formulation (Figure 14).

Based on this result, we conclude that the feasibility of low power combustible gas microsensor based on the proposed sensor platform was unequivocally demonstrated both at Synkera and independently at MSA. Phase II will target greater response via further catalyst development combined with the optimization of AAO substrate and design.

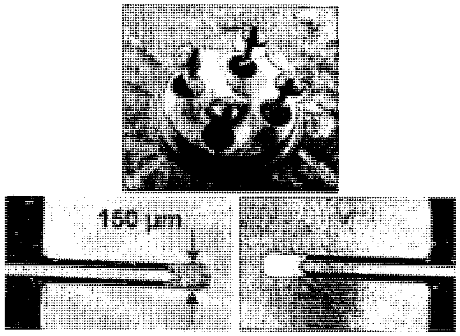

Figure 12. Prototype of the low power sensor and close up of the sensing and reference elements.

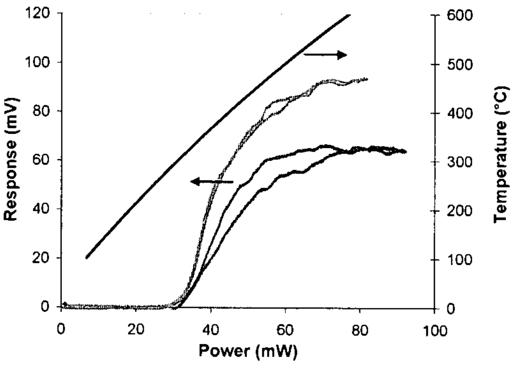

Figure 13. Response to 2.5% CH4 vs. power for two different designs.

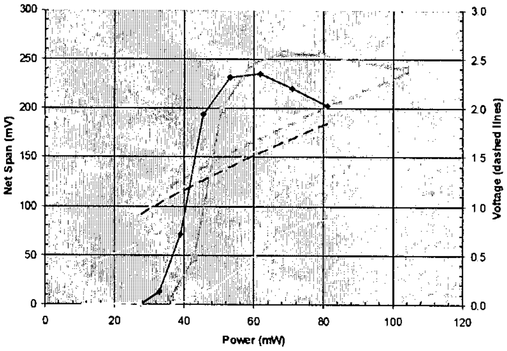

Figure 14. Response to 2.5% CH4 vs. power for design #2.5 with MSA proprietary catalyst.

4.5 Sensor Performance Evaluation.*

The testing was done both in single and in dual element (bridge) configurations using the electronic sensing module developed in this project (see next section, Figure 18, Figure 19). The test protocols met or exceeded industry standards. All work using hazardous gas mixtures was performed in fume hoods in compliance with Synkera safety policy. The data presented below are typical and reproducible, with 3 to 5 sensor tested in most experiments.

- *Sensitivity.* Sensitivity to two combustible gases, methane and propane, was determined by measuring response to different concentrations. The highest sensitivity obtained without amplification was 100 mV/%CH_4 (with MSA catalyst). The sensitivity of 50 mW sensor (with Synkera catalyst) measured using Synkera board was up to 1V/%CH_4. These values are more that sufficient for enabling the required performance of Smart Gas Card.
- *Selectivity.* Selectivity and interference with methane detection was evaluated for the following gases relevant to mining environment (methane, propane, kerosene vapor (=diesel fumes), water vapor, CO_2, CO, NO_2 and H_2S) their mixtures.
    - *Combustible gases.* Sensors had non-linear response to *propane*, with response saturating at above 0.8%, and a very small response to *kerosene*. As expected, the responses in mixtures of methane-propane and methane-kerosene were cumulative.
    - Sensors had very low response to *humidity* (dry to ~85% RH); with response to methane reduced by ~ 10% at 85% RH. This effect was fully reversible, with fast recovery.
    - *No interference* with was found for 2500 ppm CO_2, 117 ppm CO and 4 ppm NO_2.
- *Resistance to poisoning by H_2S.* The response to methane after a 5 min exposure to 5 ppm H_2S was smaller and slower than before the expose, but the sensor fully recovered (Figure 16, left).

After a 10 min exposure to 10 ppm H_2S, the sensor response time recovered but the magnitude of the response was reduced by ~20%. Heating to ~600°C did not reverse the poisoning.

- *Advanced Operating Modes.* The low thermal mass of the developed microsensors enables a very fast heating/cooling rate, which is unavailable with conventional sensors. In temperature pulse mode, when heater voltage was stepped between three values (1, 1.3, 1.8V), the current response for combustible gases was very different (Figure 16, right), enabling discrimination of these combustible gases.
- *Response time.* In temperature pulse mode, the time to reach 90% of both the heater temperature and the sensor response in the presence of 2.5% of CH_4 was as low as 0.2 seconds.
- *Long-Term Stability.* Several sensors (coated and uncoated with catalyst) were tested for microheater resistance stability for at least 2 months. The resistance of the coated microheater initially increased in comparison with uncoated one. However, after ~10 days the resistance drift stabilized and became virtually identical for both elements, ensuring stable sensor operation in a bridge circuit. During the Phase II, we will evaluate approaches to either accelerate or eliminate the initial increase in resistance of coated sensors.

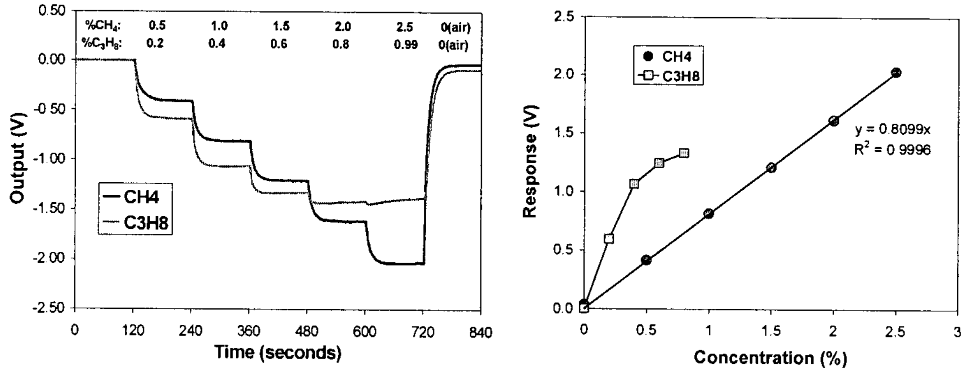

Figure 15. Typical response to step changes of methane and propane concentrations (left) and sensitivity chart (right) for low power sensor (2.1 design) tested with Synkera module.

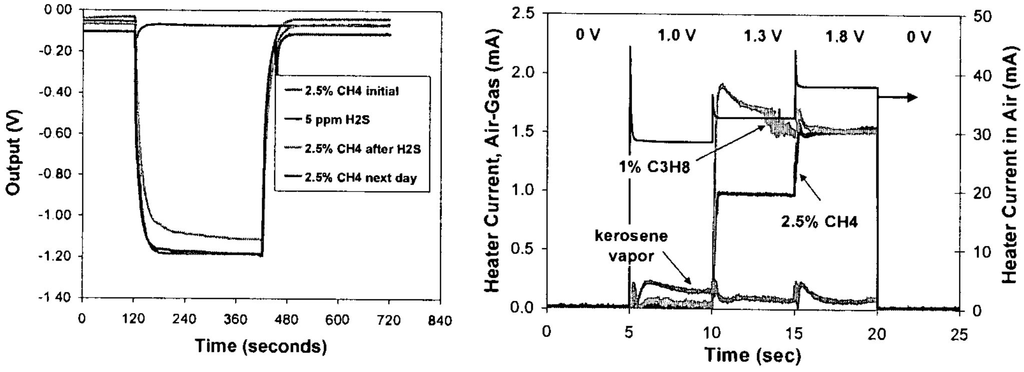

Figure 16. Left: sensor response to 2.5% CH_4 before and after 5 min exposure to 5 ppm H_2S. Note complete recovery by the next day. Right: Sensor response to different gases in temperature pulse mode. This response pattern is sustainable and reproducible over a large number of cycles (over 100 cycles tested).

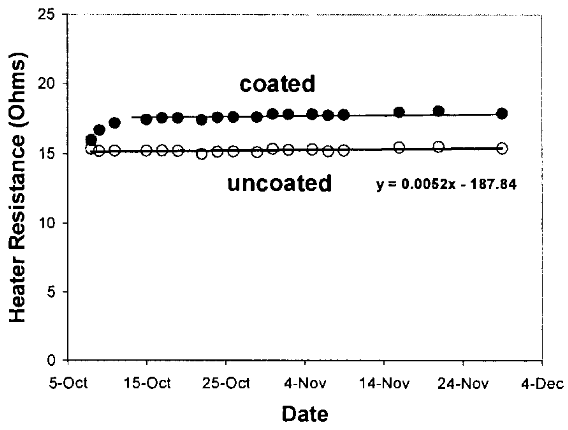

Figure 17. Long term stability of the low power microheater resistance (average of 7 sensors).

4.6 Application Development – Smart Gas Card.*

The main goal of this task was to establish target specifications for combustible gas microsensors and their associated electronic support systems. This work led to the development and implementation of a low-cost, high-performance sensing module (Figure 18), which is a starting point in the development of the Smart Combustible Gas Card™ prototype in Phase II.

Virtually all commercial pellistor-based sensing systems use bridge-based ratiometric circuits for measurement of the resistance change that occurs in the active pellistor element when combustible gas is present. A combined electronic-thermal model was created for such a circuit to approximate the performance of microsensors as a function of both circuit type and circuit element values. A bridge circuit that could support both a constant voltage and constant-current mode of operation was designed and built. The bridge balance voltage is amplified with adjustable gain (G=18 to 50) to handle variations in sensitivity. The applied voltage, current draw, and bridge output signals are available on an external connector for interfacing to a data acquisition system.

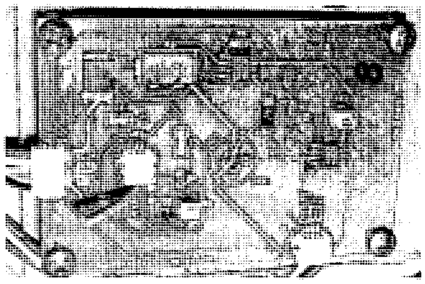

Figure 18. Combustible gas sensor support circuit (2”x3” SMT PCB).

Eight circuit cards were combined to form the basis for a combustible gas testing system (see Figure 19). The control inputs and signal outputs from each circuit card were supplied to a DAQ card embedded in a desktop computer. A LabVIEW program for data acquisition and control of all eight cards was written and used for simultaneous testing of up to 8 microsensors.

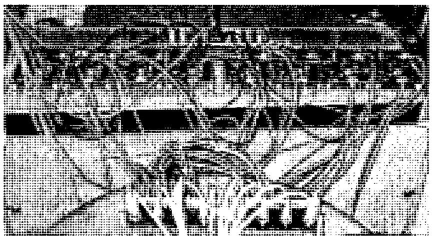

Figure 19. Eight sensor test system.

The developed support circuit forms the “front-end” electronics for the portable combustible gas sensor monitor to be designed and fabricated in Phase II. Low supply current was targeted in the circuit design to support eventual portable operation with battery power: the non-heated portions of the design draw approximately 500μA continuous, which is very small compared to the currents required to operate the microsensor. Cost of the circuit in quantities of 1000’s is estimated at $10.25, which is well within the cost targets for the Smart Gas Card.

Synkera has discussed the proposed development effort with a number of potential partners. Based on these discussions, as well as the analysis of competitive products and the sensor performance achieved in Phase I, the target specifications for Smart Combustible Gas Card have been developed (Table 2).

Table 2: Target Specifications for Smart Combustible Gas Card™

Parameter	Value	Parameter	Value
Size	3.2 x 2.1 x 0.125 in	Continuously On	Yes
Weight	< 25 grams	Confidence Indicator	Green LED every 30 sec.
Nominal Range	0-100% LEL (0-5% volume)	Numeric Display	Optional LCD
Resolution	± 1% LEL (0.01% volume)	Visual Alarm	Red LED
Factory Low Alarm	15% LEL	Audio Alarm	75-80 dB @ 1ft
Factory High Alarm	30% LEL	Vibratory Alarm	Optional
Datalogging	Optional	Self Test	Visual (LED)
RFI Protection	Yes	T-90 response time	<15 seconds
Power Required	rechargeable battery	Temperature Range	-20 to +50°C (-40 to +50°C for short excursions)
Battery life	> 1 week (10% duty cycle)	Humidity Range	0 to 95% RH, non-condensing
Approvals	US UL 913, Class 1, Div. 1, Groups A, B, C, D. Also European, Canadian will be sought		
Price	<$50	Operating Life	24 months

5. IP PROTECTION.*

The combustible gas microsensor that was demonstrated during Phase I project is based upon a patented Synkera sensor microsensor platform [17], in combination with new design, catalyst materials, and processing methods developed under this project. In addition, a patent application on the Smart Gas Card Concept, related to H_2S detection via an electrochemical sensor, is pending. In reviewing the IP landscape in this area (open literature, patents and patent application), we believe that we have developed a unique technology that offers the opportunity to successfully pursue a strong patent application. As we move forward with sensor development, we will consider whether to file for a more specific patent on this particular sensor technology, to complement the broad patent already granted. We may elect to retain some enabling details of the sensor design and fabrication as trade secrets in lieu of patenting.

6. PUBLICATIONS.

No publications have resulted from this work. As a private, for profit company, Synkera does not typically publish results this early in the development cycle. Synkera may publish or present the results of this work after appropriate steps have been taken for IP protection and product development is well under way. NIOSH support of this technology will be acknowledged in any publications.

7. MATERIALS AVAILABLE TO OTHER INVESTOGATORS

Under this Phase I project, Synkera did not plan to provide any data or research materials, protocols, or other information to investigators in the public domain. Under non-disclosure agreement, Synkera provided prototypes of the low power sensors to select customers, as well as shared the technical data on sensor performance with other current and potential partners. Once any appropriate steps have been taken for IP protection and the technology moves into the product development phase, relevant technical information (Technology Profile, Data Sheets, Application Notes etc.) will be provided to the end users and released through Synkera's website.

8. FEASIBILITY SUMMARY.*

Development of products based on nano- and microfabrication with nanoporous anodic alumina is one of the strategic efforts at Synkera [29]. Using this technology, Synkera develops and manufactures highly innovative yet practical nano- and microstructured materials, components and devices, focusing on chemical sensors [17], ceramic membranes, fuel-processing components, energy-conversion materials, and ceramic MEMS devices. Several types of sensors have been implemented using AAO as a platform, including humidity sensors, conductimetric metal oxide sensors, flexural plate wave sensors and, in this project, ***combustible gas sensors.***

The key sensor performance milestones, critical for enabling portable gas monitors and for the Phase I project to be considered a success, were achieved:

- Catalytic gas sensors with power consumption of ~50 mW at 500°C were built and tested, opening the field for development of novel Smart Gas Card personal monitors.
- Catalyst and application methods were developed and the resulting sensors demonstrated high sensitivity to methane. Phase I results (40mV with Synkera generic catalyst, 100 mV/% with MSA catalyst) are close to the originally set target of at least 100mV/%CH_4.
- Evaluation of operating modes resulted in a basic understanding of the advantages of pulsed heater mode for both increasing the discrimination capabilities and enabling long battery lifetime in portable detectors such as Smart Gas Card.

The results of our Phase I and related work have clearly demonstrated the feasibility of combustible gas microsensors and confirmed their strong competitive advantages of versus conventional sensors, with particularly strong benefits in high sensitivity and selectivity, low power consumption, chemical and mechanical stability and fast response. These features make it possible to develop novel small, lightweight and affordable gas *detectors for personal protection in hazardous environments.* The Phase II project will advance the sensor technology to a readiness level sufficient for incorporation of the sensors in such detectors, and will develop prototype version of the detector.

These sensors and detectors have a clear potential to impact both mining safety practices and as well as the industrial health and safety market in portable and fixed installations. If successful, it will allow mine operators to comply with and exceed currently updated federal safety regulations by equipping every miner with personal multigas detector at a significantly lower cost.

In summary, both projected and demonstrated cost/performance benefits are more than sufficient to justify aggressive development of application-specific products and rapid scale-up. The Phase I results form a solid framework for a comprehensive Phase II development effort focused on prototyping/demonstration/validation to set the stage for Phase III commercial production of high-performance, durable Smart Gas Card detectors that can significantly improve mining safety, save lives and address significant market needs.

9. COMPANY IMPACT AND PRODUCT STATUS.*

The Phase I of this project resulted in significant progress towards the development of a new generation of low power microsensors and affordable, reliable and portable hazardous gas detectors for personal safety. The Smart Gas Card™ family of products are a line of personal monitors, each the size of a credit card, that are small, lightweight, and unobtrusive to wear. Such innovations in sensor technology allow the fabrication of devices inexpensive enough that everyone entering a hazardous environment can wear one. This development of such an easy to use and wear personal monitor for the detection of hazardous gases will increase the use of personal protection and provide a substantial benefit to national health and safety.

The impact of this project on Synkera is in advancing our combustible gas microsensor technology to the point where it is now positioned for rapid product development and commercialization of new Combustible Gas Microsensors, *Smart Combustible Gas Cards and Multigas Cards* for mining and other applications. A low power combustible gas microsensor is the missing link that is preventing this type of personal monitor from being commercially available today. The development of such a sensor will both benefit from and fill an important gap in Synkera's expanding Smart Gas Card product line enabled by our family of low power sensors. This effort is spearheaded by the Smart H_2S Card^{TM}, which is expected to reach the market in 2008. Combined with the planned addition of a carbon monoxide sensor and an oxygen sensor, this project will also enable a family of unique multigas personal monitors. The availability of such instruments, both from a size and a cost standpoint, will lead to a revolutionary new approach to alleviating intrinsic hazards of mining industry by providing every miner with personal safety tools.

We are working with some of the leaders in the gas detection and industrial health and safety industry (including Scott Health and Safety, MSA, Detector Electronics, Sperian (formerly Biosystems), 3M, Industrial Scientific Corp, Net Safety Monitoring and others) to refine performance and cost targets and to facilitate market introduction (see Phase II Commercialization Plan for details). During Phase I Synkera already produced and sold to Mine Safety Appliances for evaluation 50 prototype combustible gas microsensor substrates.

Several of these gas detection companies have already expressed substantial interest in this proposed sensor (see letters of support), and will contribute in-kind and direct financial and marketing support to further development and commercialization. Synkera is already actively seeking investments to fund the launch of the Smart Gas Card product line.

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