# Application of Micro- and Nanotechnologies for NDIR-Gas Measurements in Harsh Environments

Buchner, Rainer[a]; Stolberg-Rohr, Thomine[a]; Pihl, Kenneth[a]; Hansen, John S. [a]; Tojaga, Senad[a]; Krishna, Arun[a]; Bergmann, René[b]; Jakobsen, Mogens H.[b]; Moos, Henrik G.[a]; Jensen, Jens M.[a]
[a] Danfoss IXA A/S, Ulvehavevej 61, DK-7100 Vejle, Denmark
[b] Department of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345 East, DK-2800 Kongens Lyngby, Denmark

## Abstract

Danfoss IXA A/S has developed a new infrared gas sensor technology for the simultaneous measurement of relevant parameters for climate and emission control such as temperature, humidity, $CO_2$, $NO_x$ and other gasses in harsh environments or in other words as close to the source of emission as possible. Exact determination of these parameters to improve climate and process control enables significant energy savings and reduction of emissions.

By combining highly sensitive multi-channel thermopiles with fast infrared emitters and specific nano-structured protective sight glasses, determination of these parameters is possible in environments where other systems fail due to e.g. contamination and corrosion. Functional prototypes of this technology have been developed and successfully tested.

The target application areas and their harsh environmental conditions demand special understanding of the characteristics of the components implemented into the sensor system in order to cope e.g. with severe temperature changes. Therefore, the characteristics of infrared sight glasses, thermopile components and infrared emitters available will be described and reviewed in this paper.

## The sensor concept

The Danfoss IXA Multigas sensor is based on the commonly know NDIR technology [1]. Gasses and gas concentrations are characterised by absorption of infrared radiation at their specific wavelength. Key components of the system are an infrared emitter with almost black body emission properties as well as miniaturised and highly sensitive multi-channel thermopile detectors. Both components are commercially available state-of-the-art devices. Each channel of the detector is equipped with an IR-band pass filter in order to limit the radiation absorbed to the wavelength range where the molecule-specific absorption takes place. The sensor is set up as a single-path, multi-beam NDIR system meaning that there is a single IR-emitter but at least one suspect as well as reference channel in order to reduce drift of the system and to compensate for impact of environmental parameters such as fluctuations in temperature of the environment or the IR-emitter. Such fluctuations could be fully compensated if there was not a spectral shift of the distribution of the IR-radiation according to Wien's law. The impact of this shift can be limited by the new and patented filter concept [2] of Danfoss IXA.

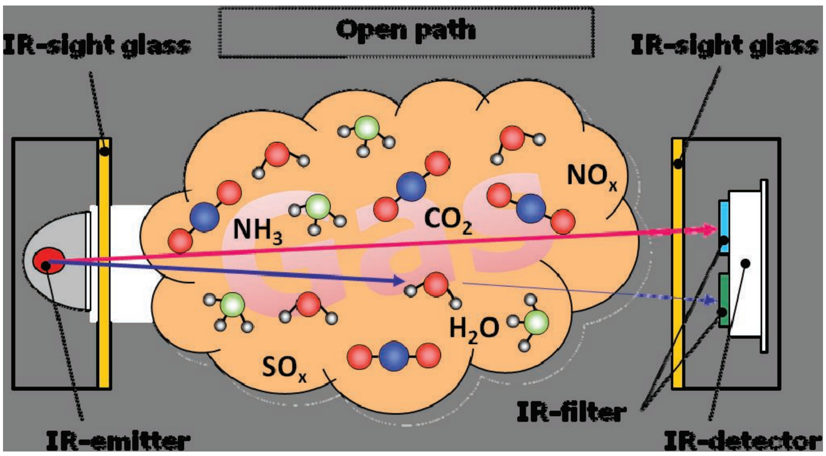


*Figure 1: Principle of the sensor setup.*

The second major improvement of the system compared to state-of-the-art environmental gas sensors is the open-path concept that is sketched in Figure 1. The IR-emitter and the detector on the other hand can be separated and protected from the harsh environment by sight glasses. Besides their optical properties these sight glasses possess specific material properties in order to provide long-term stability of the system together with less maintenance needed. The functionality of such sight glasses will be described in more detail in the following section.

Prototype sensor systems have been realised being capable of measuring $CO_2$, humidity as well as temperature for control of indoor climates in agricultural and marine applications. It could be shown on the measurement of $CO_2$ and humidity that the systems can compete with commercially available sensors regarding resolution and accuracy as shown in Figure 2 and Figure 3 below. Potential for even further improvement e.g. by optimisation of the IR-optics already has been identified and is about to be implemented.

Feasibility of the sensor concept has been demonstrated in field-tests over duration of more than 1.5 years and are still ongoing in marine applications where commercially available systems failed due to high level of vibration, dirt and salty atmosphere. Field-tests in agricultural applications, such as climate control of pig and poultry houses have been initiated as well.

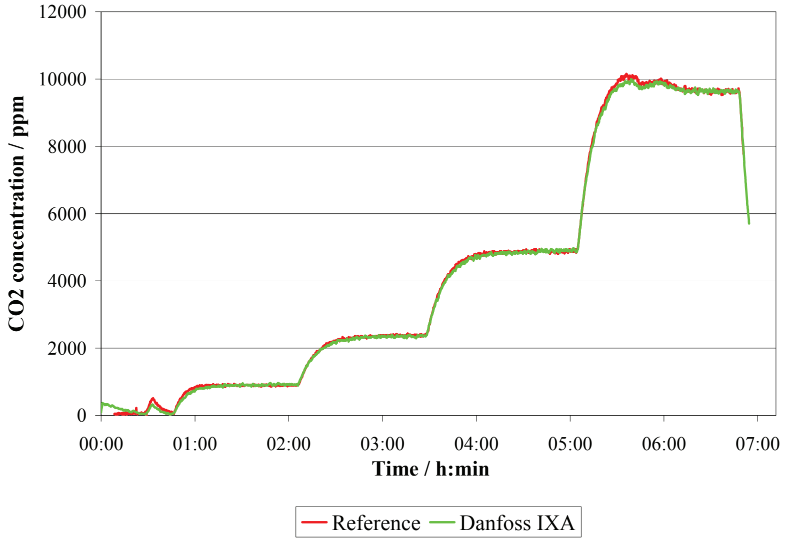


*Figure 2: Reading of the $CO_2$ concentration of the Danfoss IXA sensor plotted together with the reading of a reference sensor for comparison.*

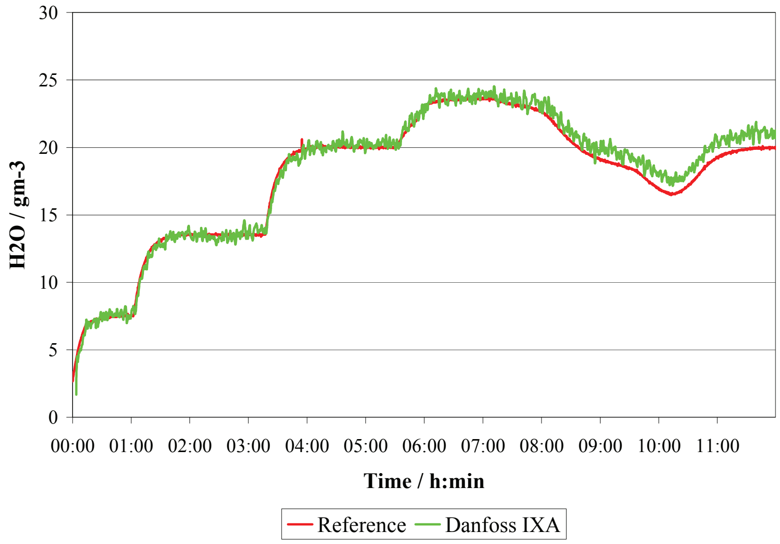


*Figure 3: Comparison of the results of a $H_2O$ measurement achieved by the Danfoss IXA sensor and a commercially available reference. The reading is given in absolute humidity.*

**Sight glass**

Optical windows or infrared sight glasses are used to shield the sensible sensor components and electronics from the harsh environment, see Figure 1. Hence, these sight glasses have to possess special properties such as high optical transmissivity in relevant infrared wavelength ranges, a superhydrophobic and “self-cleaning” surface to avoid water film formation and particle contamination, as well as thermal, mechanical and chemical long term stability in hash environments.
Commonly used materials for optical windows in state-of-the art NDIR systems are among others zinc selenide (ZnSe), zinc sulphide (ZnS), germanium (Ge), sapphire ($Al_2O_3$), gallium arsenide (GaAs) and silicon (Si) [3, 4] . Of these materials silicon could be the most favoured material. Even if it shows a lower mechanical durability compared to sapphire which is close to that of natural diamond [5], silicon can cover a much wider spectral range than sapphire, up to 15 µm instead of approx. 5 µm in case of sapphire. Silicon is, compared with other infrared window materials relatively inexpensive, enabling wide spread use in low cost civilian applications.

One drawback of silicon is the strong loss (up to 50%) of transmitted IR light due to reflection [3]. Thus, multilayer thin film antireflective coatings are applied to increase the transmissivity of sight glasses. Such antireflective coatings often combine the improvement of the optical properties with improvement of durability and chemical stability. Silicon is very stable against thermal shocks due to the very high thermal conductivity of the material while germanium and sapphire are much more susceptible.
As mentioned, by implementing “self-cleaning” mechanisms on the sight glass, the long-term stability in environments with a lot of dirt and particles can be improved. An approach to achieve “self-cleaning” surfaces on optical windows is inspired by nature and today commonly known as the “lotus effect” [6, 7]. It basically involves the formation of non-wettable superhydrophobic surfaces by minimizing the adhesion of water and solid contaminations due to an extremely reduced contact area and a decrease of the surface energy. Contaminations and particles are picked up by water droplets rolling off the surface or can be driven off by other forces such as vibration or air-flow.

DTU Nanotech has fabricated nanostructured infrared silicon sight glasses by means of reactive ion etching (RIE) in an easy and cheap single step mask-less process. As depicted in Figure 4, sub-wavelength nanostructures characterised by a random distribution and a certain range of the geometrical dimensions were created. By applying an organic coating (perfluorodecyltrichlorosilane, FDTS), the intrinsic water repellent “self-cleaning” property of the nanostructured surface could be enhanced, resulting in a static water contact angle of more than 170° and a roll-off angle lower than 1°. Moreover, an enhancement of the transmissivity of the silicon sight glasses for certain wavelength ranges due to the “moth eye” effect [4, 8] resulting from the sub-wavelength nanostructures could be demonstrated [9].

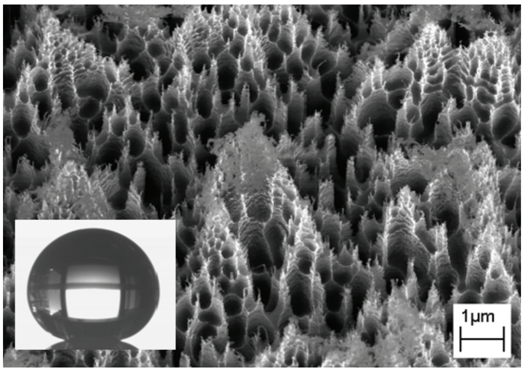


*Figure 4: SEM image of the surface of a nanostructured silicon sight glass. The inset shows a water droplet on the superhydrophobic surface characterized by a static water contact angle of more than 170° and a roll-off angle lower than 1°.*

**Thermopiles**

First miniaturized thin-film thermopiles have been presented in the 80s [10] and temperature measurements have been the driving application. It is common to use single-channel thermopiles as IR-radiation thermometers. Dual or even quad-channel thermopiles, meaning several thermopile detectors and corresponding IR-filters mounted to a single TO-package are used in most NDIR-gas sensor devices. This allows a suspect and a reference measurement for compensation purpose, like it is done with the special patented filter setup in the Danfoss IXA multigas sensor, or even the detection of multiple gasses.

Thin film thermopiles available on the market can be divided into two groups, based on the materials used. The majority of the detectors, especially for the low-cost mass market use p- or n-doped polycrystalline silicon as thermoelectric material while high-end systems are based on semi-metals and their alloys. The thermoelectric figure of merit Z is used for comparison of thermoelectric materials and is defined as: $Z = \frac{\alpha^2}{\lambda \cdot \rho}$, with α being the Seebeck coefficient, ρ the resistivity of the material and λ the thermal conductivity. These parameters are listed in Table 1 below for n- and p-type polysilicon, aluminium - often used as second material for silicon based thermopiles - and the semi-metals antimony and bismuth and some of their alloys described in literature.

| **Material** | **Reference** | **α [µVK$^{-1}$]** | **ρ [µΩm]** | **λ [Wm$^{-1}$K$^{-1}$]** | **Z [10$^{-6}$ K$^{-1}$]** |
|---|---|---|---|---|---|
| n-Poly-Si | [11] | -100 to -500 | 10 to 1000 | 20 to 30 | 12,5-33,33 |
| $Bi_{1,8}Sb_{0,2}Te_{2,7}Se_{0,3}$ | [12] | -220 | 10,98 | 1,4 | 3148,58 |
| n-$Bi_{0,87}Sb_{0,13}$ | [12] | -100 | 7,14 | 3,1 | 451,79 |
| Bismuth | [11] | -72,8 | 1,10 | 8,1 | 594,82 |
| Aluminium | [11] | -3,2 | 0,028 | 238 | 1,54 |
| Antimony | [11] | 32 | 18,5 | 0,39 | 141,92 |
| p-$Bi_{0,5}Sb_{1,5}Te_3$ | [12] | 230 | 17,24 | 1,05 | 2922,33 |
| p-Poly-Si | [11] | 100 to 500 | 10 to 1000 | 20 to 30 | 12,5-33,33 |

*Table 1: Seebeck coefficient, resistivity, thermal conductivity and thermoelectric figure of merit of commonly used materials for thin-film thermopiles.*

Thermoelectric, thermal and electrical properties of polycrystalline silicon are highly dependent on the doping level. A high Seebeck coefficient can be reached, making the material quite attractive, taking into consideration that it is available in all state-of-the-art semiconductor/CMOS fabs. MEMS processes for bismuth and antimony have a low availability due to historical reasons and their lack of CMOS-compatibility. This has the simple effect that the process costs for such thermopiles are much higher than for standard CMOS thermopiles – on first sight at least. The figure of merit of pure antimony and bismuth is already an order of magnitude larger than for polysilicon due to the low thermal conductivity. This allows semi-metal thermopiles to be much smaller at a comparable performance. This again results in lower cost for smaller packages and smaller IR-filters that may compensate for the higher cost level of the chip.

Silicon based thermopiles characterised by a short time constant due to the high thermal conductivity of the material and their lower temperature dependency. Schieferdecker et al. [11] made measurements of the temperature coefficient of polysilicon-aluminium thermopiles which results in 0.01% $K^{-1}$. Bismuth-antimony thermopiles usually have a temperature coefficient which is one order of magnitude higher. Changes in temperature, even quite rapid ones, are one issue that characterises the field of application the sensor of Danfoss IXA is made for. The use of the ratio of suspect and reference channels equals out most of the temperature impact on the detector if the channels behave equally. The impact on inhomogenities of advanced CMOS manufacturing processes on a single silicon substrate is negligible taking only a small area – meaning neighbouring devices into consideration. The detectivity of high-end polysilicon-based thermopiles can reach up to $2.9e^8$ cm√Hz $W^{-1}$ and a sensitivity of 51 $VW^{-1}$ [13].

Bismuth-antimony thermopile detectors with a detectivity of $3.6e^8$ cm√Hz $W^{-1}$ and a sensitivity of 99 $VW^{-1}$ can be integrated on comparably small area [14].
The integration of detectors on a small area furthermore reduces impacts of thermal gradients on the detector housing caused by sudden non-uniform changes in temperature of the environment. For single detectors so-called isothermal caps have been introduced [15], but this is not available for multi-channel thermopiles yet and therefore is a small package and a small distance in between the detectors a good alternative.

Semi-metal based thermopiles do have smaller package and IR-filters and offer far better sensitivity and detectivity but are slow and comparably expensive. Silicon based devices are faster, allow higher modulation frequencies and have smaller tolerances due to the high reproducibility of standard CMOS-processes. Choice of these components always is a trade-off between cost, durability and performance and shall be made with respect to the detailed requirements and cost structure of the sensor system.

**IR-Emitter**

The IR-emitter is the second key component for the functional NDIR-sensor. Over the last decades a miniaturised light-bulb has been a simple, effective and quite inexpensive solution. The filament of these lamps is heated up to temperatures of 2000 K and above, resulting in a high level of radiation emitted at comparably short wavelength with a peak according to Wien's law at about 1.4 µm. The fact that the bulb is evacuated makes them highly energy efficient and the small thermal mass of the filament enables direct modulation. The glass envelope limits the possible applications to measurements up to 5 µm since the glass blocks radiation at higher wavelength. For the measurement of $CO_2$ and humidity that is still sufficient. Typical lifetime of these bulbs is a few thousand hours. What is limiting the lifetime is evaporation of the filament leading to a blackened envelope, decrease of emission and sudden burn-out. These light bulbs for application in mechanically demanding environments have the drawback of a comparably fragile filament. Change in position of this filament due to shock or vibration will result in a change of characteristics of the sensor system and therefore require re-calibration if the filament is not destroyed.

Micromachined infrared emitters are a potential alternative to the light bulb for integrated gas analysis systems. They usually consist of a free standing membrane structure which is heated to temperatures between 450°C [16] and 700°C [17] and is supported by a silicon frame as shown in figure 4. The heated area covers up to 3.78 $mm^2$, depending on which product is used, and the lifetime can reach more than 10 years at 50% duty cycle [16]. The heated membrane is treated with a coating to achieve almost black-body properties.

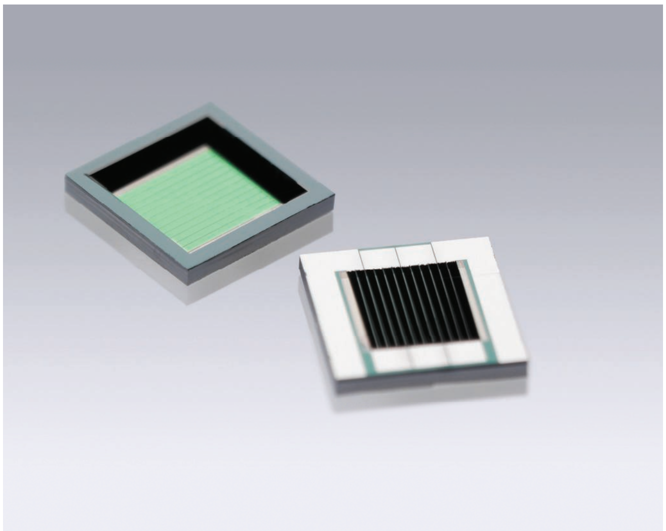

*Figure. 5: IR-emitter chip (by courtesy of Leister Process Technologies).*

These systems are mechanically robust due to the small thermal mass of the membrane and the strong support by the silicon frame. The same general mechanical setup is also used for the thermopile detectors giving them the same robustness. Drawback of MEMS based emitters is their high price level and the lower level of radiation emitted.

Schulz et al. [18] investigated the impact of environmental parameters on the stability of micromachined IR-sources. IR-sources run at constant input power do show severe fluctuations in optical output due to changes in environmental temperature as well as due to any parameters that affects the thermal losses and therefore influence the temperature reached. The heated membrane structure is more or less thermally decoupled from the surroundings, i.e. the silicon bulk material. Still about 90% of the input power is not converted to thermal radiation but simply lost due to thermal conduction and convection. As soon as these heat transportation mechanisms change e.g. due to a change in thermal conductivity of the surrounding air by a change of humidity, change of pressure or some air flow, the temperature of the source fluctuates and so does the IR-emission. It could be shown by measurements that the patented filter concept of Danfoss IXA successfully compensates the variation of temperature of the IR-emitter due to these environmental effects. Therefore expensive packaging solutions can be avoided.

## Summary

The general concept of the Danfoss IXA Multigas sensor has been introduced. The sensor is aiming at measurements of $CO_2$, humidity and temperature in demanding and harsh environments. Nano- and microtechnological components can be seen as an enabler for this technology. Key components are an IR-sight glass, micromachined thermopile detectors and IR-emitters. The characteristics of these components have been reviewed, particularly with regard to the demanding applications in order to provide insight into the detailed requirements.

Functional prototype systems have been prepared and their performance has been compared to commercially available sensor systems. We tested our sensor systems using MEMS-IR-emitters and thin-film thermopiles successfully for shock according to IEC 60068-2-27 up to levels of 100 g, 3 repetitions in each axis and direction; 25 g, 1000 repetitions in each axis and direction and for vibration according to IEC 60068-2-6 at levels of 0.7 g and frequencies of 5-200 Hz. The systems have neither been destroyed nor affected in their measurement performance and accuracy. This proves the robustness of the components and of course the robustness of the overall setup of the Danfoss IXA Multigas sensor. Systems are running in a field test for now more than 1.5 years, showing no significant drift or other degradation and the test is still ongoing.

## References

[1] Günzler, H. M. Heise: IR-Spektroskopie, VCH, 1996.

[2] J.M. Jensen, M.Y. Benslimane: Patent WO2005121751A1.

[3] D.C. Harris: Durable 3-5 µm transmitting infrared window materials, In: Infrared Physics & Technology 39 (1998), pp. 185-201.

[4] D. S. Hobbs and B. D. MacLeod: Design, Fabrication, and Measured Performance of Anti-Reflecting Surface Textures in Infrared Transmitting Materials, In: Proceedings of SPIE 5786 (2005) pp. 349-365.

[5] C.R. Seward, E.J. Coad, C.S.J. Pickles, J.E. Field: The liquid impact resistance of a range of IR-transparent materials, In: Wear 186-187 (1995), pp. 375-383.

[6] M. Nosonovsky, B. Bhushan: Superhydrophobic surfaces and emerging applications: Non-adhesion, energy, green engineering, In: Current Opinion in Colloid & Interface Science 14 (2009), pp. 270-280.

[7] M. Ma, R.M. Hill: Superhydrophobic surfaces, In: Current Opinion in Colloid & Interface Science 11 (2006), pp. 193-202.

[8] S. J. Wilson, and M. C. Hutley, “The optical properties of ‘moth eye’ antireflection surfaces,” In: Optica Acta, 29(7) (1982), pp. 993-1009.

[9] R. Bergmann, Z.J. Davis, M.S. Schmidt, S. Clausen, A. Boisen, J.M. Jensen, R. Buchner, T.Stolberg-Rohr, M.H.Jakobsen: Development of nanostructured protective „sight glasses“ for IR gas sensors, SPIE, Defence, Security+Sensing (2011), to be published.

[10] T. Elbel, J. Müller, F. Völklein: Patent US 4.665.276 (1987).

[11] J. Schieferdecker, R. Quad, E. Holzkämpfer, M. Schulze: Infrared thermopile sensors wit high sensitivity and very low temperature coefficient, In: Sensors and Actuators A 46-47 (1995), pp. 422-427.

[12] F. Völklein, A. Wiegand, V. Baier: High-sensitivity radiation thermopiles made of Bi-Sb-Te films, In: Sensors and Actuators, Vol. A29 (1991), pp. 87-91.

[13] HTS E31 Multichannel Sensor, Datasheet, Heimann Sensor GmbH (2011).

[14] Four Channel Thermopile TS4x2001/TS4x200x, Datasheet, Micro-Hybrid Electronic GmbH.

[15] M. Liess, H. Karagözoglua, H. Ernsta: Reducing thermal transient induced errors in thermopile sensors in ear thermometer applications, In: Sensors and Actuators A154 (2009), pp. 1-6.

[16] Infrared sources catalogue, Leister Process Technologies, Axetris Division (2011).

[17] Pulsed Broadband Infrared Light Source MIRL 17-900, Datasheet, Intex (2011).

[18] O. Schulz, G. Müller, M. Lloyd, A. Ferber: Impact of environmental parameters on the emission intensity of micromachined infrared sources, In: Sensors & Actuators A 121 (2005), pp. 172-180.