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Gas-Selective Optical Sensors for Fire Detectors

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Abstract: At the Center for Chemical Sensors (CCS) of ETH-Zürich, gas-sensitive membranes have been developed during the last three years. In co-operation with Pentapharm AG, Basel, and Bosch Telecom GmbH, Frankfurt, the research has led to the development of a world novelty, a gas-selective fire detector called MagicSens. Compared with conventional fire detectors this reacts specifically to combustible gases and considerably reduces thereby the false alarm ratio and the subsequent associated costs. Additionally, since combustible gases such as NO_2 are produced during the whole first phase of a fire, the fact that the membranes are very sensitive means the alarm time could be shortened. The signal transduction in the sensor can be produced with cheap optical items, such as LED and photodiodes. The new fire detector will, therefore, not be more expensive than a conventional one. The product is due to be launched on the market in the near future.

Keywords: Ammonia · Chemical sensor · Fire detector · Nitrogen dioxide · Optical gas sensor

1. Introduction

For the analysis of volatile compounds, physico-chemical sensors can be used as alternatives to gas chromatographs (GC), ion mobility spectrometers (IMS) and quick tests based on test tubes such as those from Dräger [1]. Typical gas sensors are generally classified according to type of transducer into electrochemical, optical, calorimetric/thermal, gravimetric, magnetic sensors [2] and others, *e.g.* acoustic wave sensors [3]. The largest group of gas sensors are the solid state sensors based on metal oxides and includes sensors using various transducers [4].

1.1. *Micro Sensors, Sensor Arrays, and Electronic Noses*

There is an increasing demand for micro sensors and sensor arrays for gas analysis. Applications include early recognition of cable fires, the protection of buildings and their inhabitants, monitoring industrial processes, checking products and their packaging, as well as medical applications such as monitoring blood gases and CO for premature babies. For well-defined applications, chemical sensors provide attractive solutions because they are economical, easy to use and small. Miniaturization, where single sensors have been combined in arrays to form, *e.g.* electronic noses, offers a further advantage.

Electronic noses either comprise relatively unspecific gas sensors which consist of metal oxide semiconductors [5], or contain specific types of transducers coated with polymer films or thin films of chemical compounds such as porphyrins [6] and phthalocyanines [7]. In the case of metal oxide semiconductors, the recognition process is based on the applied potential resulting from oxidation or reduction of the analyte relative to the adsorbed oxygen. In sensors coated with specific films, sorption of the analyte only changes the physical properties of the film [8]. Changes in the physico-chemical properties of the sensitive layer can be measured in terms of conductance, impedance, changes in visco-elasticity and density, mass enhancement, heat transfer or general changes in surface structure.

In addition, there are well-established gas sensors which exhibit a modest selectivity related to the applied potential consisting of amperometric devices [9]. They rely on an electrochemical reaction of the electroactive analyte in an internal buffer solution. Most of these sensors are complex to construct and their detection limit is too high for many applications, but an exception is described in [10].

1.2. *Optical Gas Sensors*

The number of optical gas sensors currently available is still small. The very first 'optodes' were generally based on the incorporation of pH-sensitive dyes in polymer layers. On exposure to gases which are acidic, such as CO_2 and SO_2, or basic, such as NH_3, protonation and deprotonation of the dyes occur, with a subsequent change in the absorption spectrum [11]. Later developments involved research on modifying the optical transducer principle, ranging from measurements of simple absorbance to assessments of luminescence resonance energy transfer [12]. However this type of 'optode' still exhibited poor selectivity.

In contrast, optical O_2-sensors based on the quenching of the luminescence of a ruthenium(II)-diimine dye by oxygen is an example of a very selective sensor [13]. These 'optodes' were first described in 1968 by Bergman [14], who used them in physiological investigations.

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Later, the specific complexation reactions of the target analyte with complexing agents were taken into account in order to enhance the selectivity of the sensors. In the group of W. Simon, selectivity together with optical transduction was achieved by combining a lipophilic pH indicator, a so-called chromoionophore, and an ionophore [15]. In this way, the information yielded from the host–guest interaction was transformed into an optical signal [16]. The chromoionophore changed its absorption spectrum due to an acid–base reaction. In the case of a solvent polymeric NH_3-selective sensor layer, ammonium ions were formed by deprotonation of the chromoionophore. The NH_4^+ ions were complexed by using ionophores with different stability constants and these reactions were used to determine the mass balance. The stability of the complex and the pK_a of the indicator together influenced the dynamic range of the optode [17].

In order to investigate the sensing principles for neutral analytes, their nucleophilic addition to trifluoroacetaniline derivatives, so-called reactands, was studied. Upon coupling such reactands to a chromophore, the conjugated system was elongated and the nucleophilic addition was followed by a broad hypsochromic spectral shift in the visible range. Optical sensors, incorporating chromoreactands in a plastified polymer film, responded with a reversible reaction either to alcohols [18], amines [19] or aldehydes [20]. The analyte concentrations in the gas phase and the related signals were correlated by means of optical spectroscopy [21]. A comparable reaction was investigated where a benzaldehyde derivative was added to enhance the selectivity of an SO_2-sensor [22].

The sensor array for fire detection was based on an optical sensor for NO_2, which achieves its selectivity due to the reactivity of NO_2 with aquacyanocobalt(III)-cobyrinate derivatives combined with a lipophilic pH-indicator dye incorporated into a solvent polymeric film. This 'optode' enables measurements in the ppb range [23][24]. On this basis a sensor for detecting combustion gases was obtained. In addition, an optical sensor, a NH_3-selective optode, was developed for detecting NH_3, a typical interfering gas. This sensor allows the discrimination of cigarette smoke, distinguishing it from any other combustion smoke, which means the number of false alarms can be reduced. At Bosch Telecom GmbH, a number of other sensors, *e.g.* for CO_2 and CO which are produced during combustion, have been tested. These sensors were provided by other research groups and are under consideration for implementation in fire detectors [25].

1.3. *Fire Detectors with Optical Gas Sensors*

Current fire detection systems are designed to respond to the smoke or heat generated during smoldering and flaming combustion. Fire alarm sensors can be installed in various places under different conditions, but they should, of course, work properly and be failure-free. Smoke aerosols are commonly detected using stray-light sensors and ionization chambers. In reality, interfering particles like dust induce unintentional signals. Therefore about 20% of alarms are false alarms (Frankfurt Airport [25]). Efforts to improve the sensors using intelligent algorithms have improved their reliability to such an extent that it takes 100 years, on average, for such a fire detector to produce one false alarm. Although this is an improvement, the number of detectors installed per object puts this figure into context. For instance, at Frankfurt Airport there are 65,000 fire detectors installed, and the fire brigade has to deal with more than 2,000 false alarms per year. This raises the costs, which could be largely avoided if more reliable fire detectors were constructed. If traditional fire detectors were additionally equipped with gas sensors, which react selectively to combustion gases such as CO, CO_2, NO, NO_2 and H_2, and do not react to ammonia or particles, it would be possible to avoid most false alarms. So far installing commercial gas sensors in conventional fire detectors has not been widely applied owing to the high power consumption of these devices, their cross-sensitivity, short life-times and the high price of currently available gas sensors [25]. The power consumption for each detector must be limited to 2 mW because the whole system must be guaranteed to run for 72 h in order for an emergency power supply to cover the period of a power cut. For this reason, optical gas sensors, which have very low power consumptions and require low-priced components, such as photodiodes, LEDs and polymer layers, seem to be very promising.

For these reasons, the joint project of CCS, Pentapharm AG and Bosch Telecom GmbH has led to a leap in the technology of fire detection. It has developed a novel technology to selectively recognize combustion gases which has a low energy uptake (0.4 mW) and only moderate costs [26]. By combining these new sensors with conventional fire detectors, false alarms are, as a matter of principle, excluded. Additionally the time taken to detect a fire has been reduced by up to 75%. This is especially significant since a fire can spread to cover double the area every minute. Therefore, the chances of being successful in the market look extremely good.

The collaboration of CCS with Bosch Telecom GmbH started after CCS was awarded the 'Technologie Standort Schweiz' prize in 1996 and had participated in the Hannover Fair in 1997.

2. Results and Discussion

If materials such as wood, cotton, polymers or organic solvents comparable to those used for test fires are burnt, a number of oxides are generated. In contrast to SO_2, CO, and CO_2, NO and NO_2 are not primarily products of the burning materials. Instead they tend to be produced from the nitrogen and oxygen in air due to the rise in temperature in the burning zone. Open fires especially *e.g.* of ethanol, produce higher quantities of NO and NO_2 (up to 2 ppm) than smoldering fires of wood [25].

Gas monitoring is also concerned with interfering gases such as SO_2 and NH_3. For SO_2, long-term contact at room temperature, which may induce such damage as corrosion, is crucial, whereas for NH_3 it is primarily cigarette smoke which can be detected as an interferent for smoke detectors.

2.1. *Optical Sensor Chip*

For the research at CCS, optical chips have been used. These consist of photodiodes and an LED integrated onto a standard housing (Fig. 1). If gas-sensitive membranes are cast onto the photodiodes then they can be used as simple absorbance measurement devices for optode membranes. Four photodiodes surrounding a red LED allow absorbance changes in the region around 660 nm to be monitored simultaneously in up to four different membranes. Such a photodiode has edges 1 mm long. The planar arrangement facilitates the production as well as the casting, while the light intensity beside the LED is still high enough.

With this setup the responses of three different optode membranes selective to various (combustion) gases can be simultaneously recorded while keeping one photodiode as a reference.

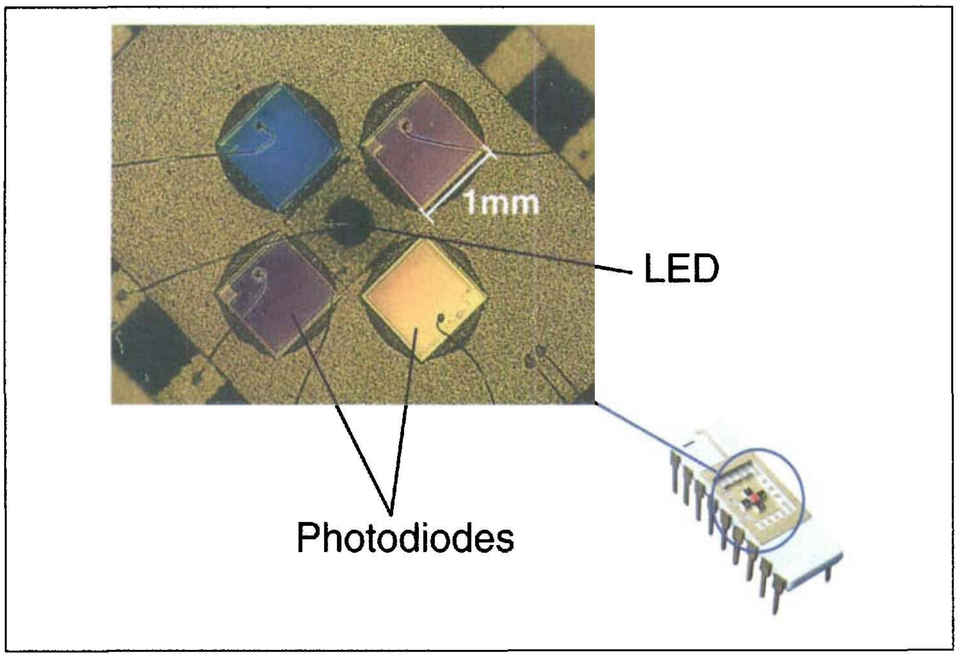

Fig. 1. Optical chip used for gas sensing at CCS, consisting of an LED as the light source and four photodiodes as detectors. The photodiodes serve at the same time as substrates for the gas-sensitive polymer layers.

2.2. *Influence of the Cobalt(III)-cobyrinate on the Sensor Response*

In discussing the reactions above, it was suggested that a nitrite-sensitive membrane, such as the one introduced by C. Demuth [27] for measuring dissolved NO_2^-, may also be used in the gas phase. The nitrite-selective membrane showed exceptional selectivity (especially to nitrate and chloride), a quick response time and a low detection limit at 10^{-5} M nitrite (0.24 mg l^{-1}). In the first experiments in a test set-up, this membrane was also shown to be very sensitive to nitrogen oxides generated by fires. Therefore further investigations were mainly based on the same composition of the solvent polymeric membrane. One membrane component, however, was omitted due to stability problems.

The sensing scheme investigated in liquid samples is based on the coextraction of a nitrite and a proton from the sample phase. Thereby the nitrite ion is bound to aquacyanocobyrinate (L, ligand) (Fig. 2). A protonation of the chromoionophore (C) occurs, which leads to a change in its absorbance spectra and provides the optical signal in absorbance or transmission changes (Scheme: a). The selectivity is introduced by complexation of NO_2^- to the metal complex. The binding of nitrite to the aquacyanocobyrinate can be studied with UV/VIS spectrophotometry since the absorption spectra of the nitrite-cyanocobyrinate complex shifts toward higher wavelengths relative to the aquacyanocobyrinate. This effect can be referred to the exchange of the water molecule in the axial position with nitrite [27][28]. Such a change in the spectra was not found in the experiments with humid NO_2.

It is assumed that disproportionation of NO_2, which is used as the analyte gas and is absorbed into the polymer layer, occurs with the water molecule of the aquacyanocobyrinate (L) (Fig. 2) to give nitric and nitrous acid. This induces a protonation of the chromoionophore (C) and results in an increase in its absorbance at 666 nm (Scheme: b). Absorbance is measured in transmission on the planar diode-sensor chip. The reaction rate of the sensor strongly depends on the amount of aquacyanocobyrinate within the membrane, whereas changes in humidity conditions have little influence on the response. Therefore, it is assumed that this species rather than dissolved water or humidity adsorbed at the surface of the film, is preferable as the water source. The reaction is not completely reversible. The high acidity of nitric acid and the consequent nitrate enrichment seem to be

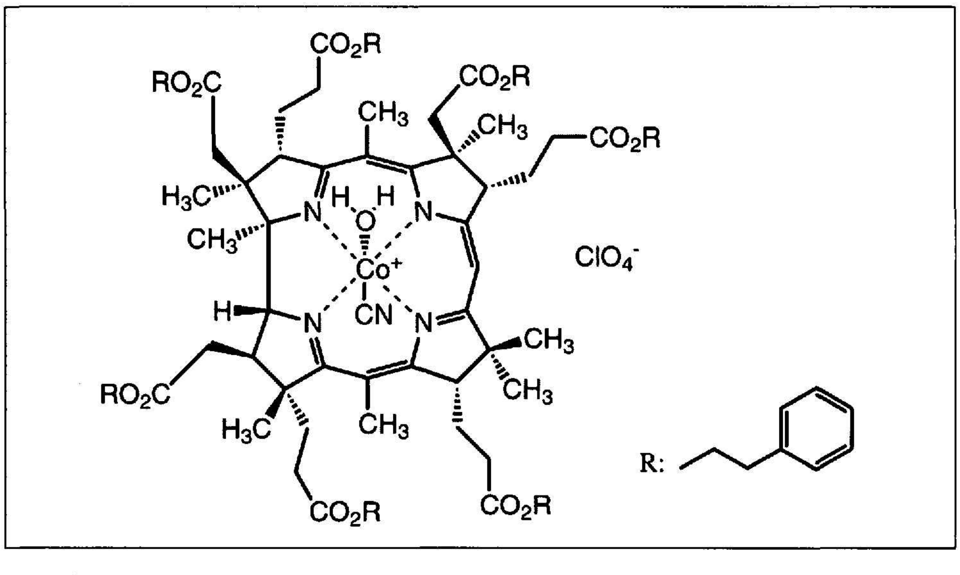

Fig. 2. Structure of an aquacyanocobalt(III)-cobyrinate derivative as used for nitrite sensing, which was incorporated into the polymer layer

a) Reaction with nitrite

$$NO_2^-{}_{(aq)} + H^+_{(aq)} + [L\text{-}H_2O]^+\cdot X^-_{(m)} + C_{(m)} \rightleftharpoons [L\text{-}NO_2]_{(m)} + CH^+\cdot X^-_{(m)} + H_2O_{(m)}$$

b) Reaction with nitrogen dioxide

$$2\,NO_{2(g)} + [L\text{-}H_2O]^+\cdot X^-_{(m)} + 2\,C_{(m)} \rightleftharpoons CH^+\cdot NO_3^-{}_{(m)} + CH^+\cdot X^-_{(m)} + [L\text{-}NO_2]_{(m)}$$

Scheme. Reactions which occur in the membrane due to exposure a) to nitrite and b) hypothetically to NO_2

the reason for this. However, the reaction mechanism with NO_2 has to be investigated further.

The sensor response is linear during the initial phase of the reaction and the slope strongly depends on the NO_2 concentration. Therefore it is possible to obtain a dynamic range of 25 – 800 ppb NO_2 within the very first seconds (Fig. 3 and 4). The NO_2-sensitive membrane was found not to show any cross-sensitivity to either NO or CO.

2.3. *Enrichment Factor, Detection Limit and Nanotechnology*

The enrichment factor of a substance in a certain medium is defined as 'the solubility of *e.g.* a gas in the polymer compared to the concentration of gas in air having the same volume as the polymer and under standard temperature and pressure' [29]. The smallest concentration we could measure with our setup was 15 ppb (which corresponds to the permitted yearly average as determined in the Swiss Clean Air Act). The membrane had a thickness of 25 µm and the concentration of the chromoionophore was $4.27 \cdot 10^{-3}$ M. 10% of this amount was protonated after exposure to a gas stream of 15 ppb NO_2 for 4 h. This concentration of NO_2 corresponds to $6.7 \cdot 10^{-10}$ M in air. Compared with $4.27 \cdot 10^{-4}$ M of protonated chromoionophore as the reaction product or as the NO_2-concentration, which was extracted into the membrane, it gives an enrichment factor of $6.4 \cdot 10^5$ (Table). This extraordinarily high value reflects the further reaction of the absorbed NO_2 whereby additional extraction of NO_2 from the gas sample into the membrane can occur. Therefore in this case the enrichment is not determined by the solubility of the analyte in the polymer layer, but rather by the equilibrium of the nitric and nitrous acid produced with water and the chromoionophore.

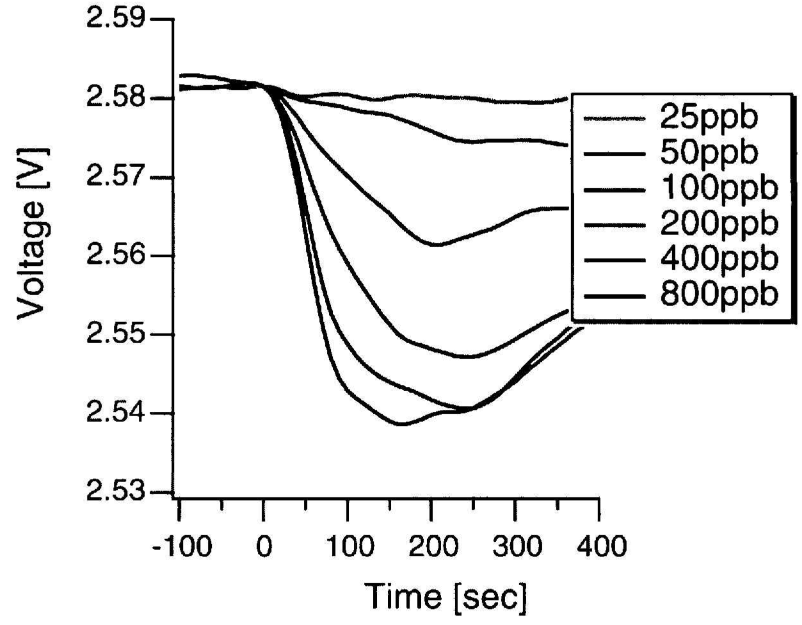

Fig. 3. Response of the optical NO_2-sensor in voltage [V] to 25 – 800 ppb NO_2 in air with 50% relative humidity and a flow rate of 50 ml/min.

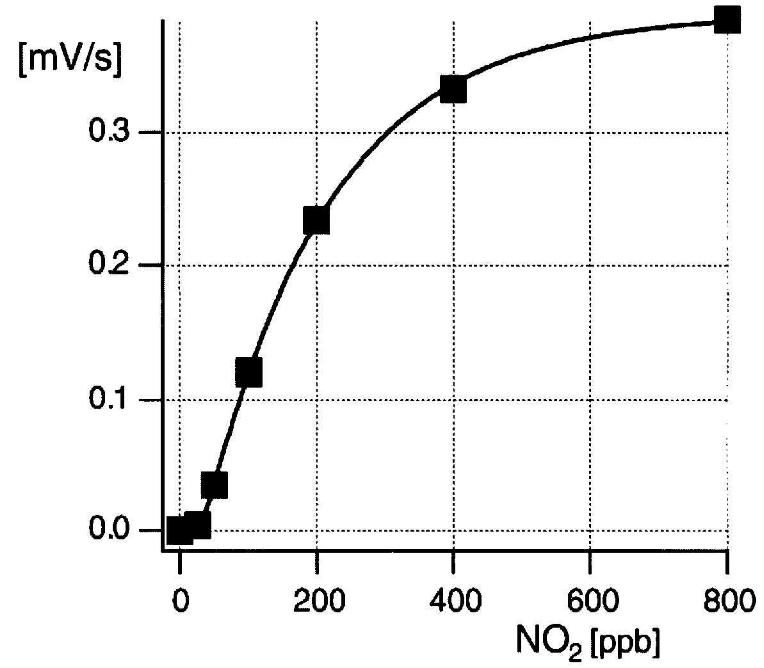

Fig. 4. Slope of the sensor response to different NO_2 concentrations within the first minute of contact.

NO_2 concentration outside:	30 µg / m^3	15 ppb
Amount of NO_2 in a volume of 25 nl:	$75 \cdot 10^{-8}$ ng	$9 \cdot 10^6$ molecules
Extracted amount of NO_2:	0.48 ng	$6 \cdot 10^{12}$ molecules
Sensitive compound within the membrane:	125 ng	$6 \cdot 10^{13}$ molecules

Table. Calculated values for a membrane with a volume of 25 nl and a gas concentration of 15 ppb NO_2.

2.4. *Flow-through Systems and Cross-sensitivity to Humidity and SO_2*

Measurements in the batch mode omitting a flow-through system can lead to a depletion of the analyte in the sample phase. When we measured the NO_2-membranes in a desiccator and adjusted the initial concentration with an inlet of a known gas volume containing NO_2, we observed a heavy dependence on the size of the sensitive area. Thus, we had to take into account not concentrations but rather absolute quantities of analyte and sensitive host molecules within the membrane.

However, for the sensor operating in a fire detector, the batch setup comes closer to real-life conditions than a flow-through system. Additionally, the influence on changes in humidity was much less pronounced in batch measurements. In the flow-through system a strong increase in absorbance was observed due to dry air. Measurements that were carried out in a desiccator with different humidity conditions, showed a negligible influence. There was a minor increase in absorbance due to increasing humidity. For membranes omitting the aquacyanocobyrinate, this cross-sensitivity was much more pronounced.

The discrimination of SO_2 is also referred to the activity of the aquacyanocobalt(III)-cobyrinate. With the batch setup the signal to NO_2 was determined to be 20 times higher than that to SO_2. Membranes where the metal complex was omitted showed a much higher sensitivity to SO_2. These results were obtained with initial concentrations of 2 and 10 ppm SO_2, compared to 0.5 and 1 ppm NO_2. With both membranes the observed protonation of the chromoionophore caused by such high SO_2-concentrations was irreversible (12 ppb is the yearly average concentration permitted by the Swiss Clean Air Act).

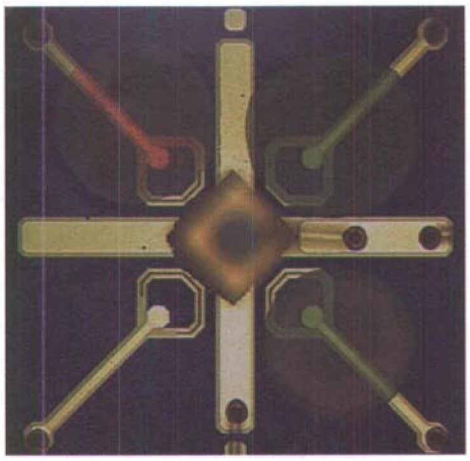

Fig. 5. Prototype of an optical silicon wafer for gas sensing with an LED in the center and with three photodiodes which are coated with polymeric membranes as used in fire detectors (Bosch Telecom GmbH).

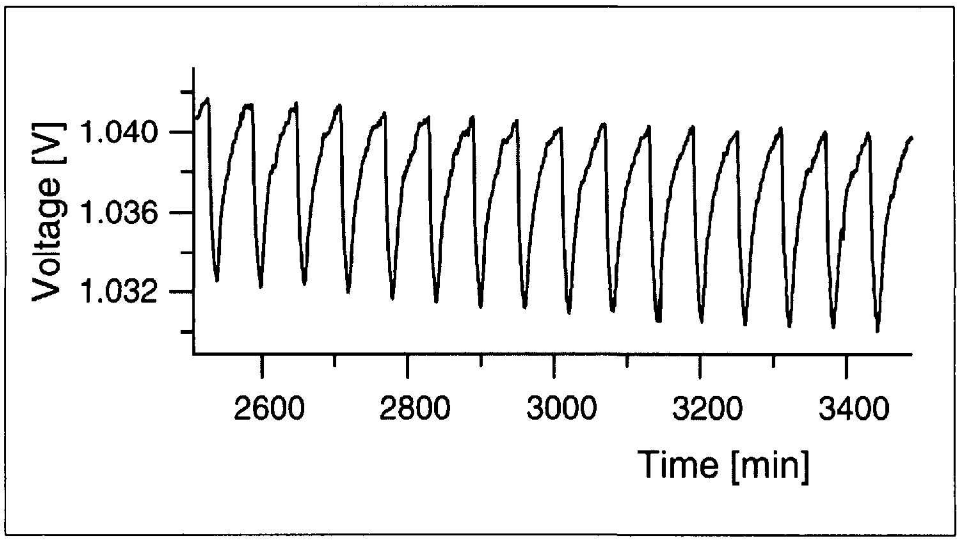

Fig. 6. Reproducibility and reversibility of the NO_2-sensor response to 1 ppm NO_2.

2.5. *Integration in a Fire Detector*

At Bosch Telecom, efforts to miniaturize the optical chip have led to a marketable silicon wafer which includes the whole optical setup within an area of only 1.5x1.5 mm. The diameter of one optically sensitive area is then 300 µm (Fig. 5). Long-term measurements were performed to test the reproducibility and reversibility of the sensor response (Fig. 6).

Several measurements were carried out to obtain approval for the application of the NO_2-sensor in fire detectors. To place a new fire detector on the market it has to pass various tests as laid down in the European norm EN 54. It was possible to demonstrate that the NO_2-sensor not only fulfils this requirement but also is even superior to optical reference systems and to the temperature probe in cases of smoldering combustion (Fig. 7 and 8). Overall, the final NO_2 concentration is between 40 ppb and 1.7 ppm, depending on the burning material.

NH_3 is released in measurable concentrations only when cigarettes and certain plastics are burnt. Thus, an NH_3-sensor like the one mentioned above could be used to discriminate cigarette smoke, which frequently gives rise to false alarms with stray light sensors.

The stability requirements for fire detectors are rigorous (European norm EN 54, part 5 and 7). For a gas sensor to be admitted to the market, an operational and shelf-lifetime of at least two years at temperatures up to 60 °C have to be demonstrated. Considerable efforts were made to reach this goal. Stress tests with NO_2-sensitive membranes have been performed exposing the polymer layers to temperatures ranging from –20 °C to 60 °C at a relative moisture content of 40% and 75% and to suspensions of bacteria and fungi, as a germ load stress test, for different lengths of time. Whereas the microorganisms had no influence on the membrane characteristics, a temperature of 60 °C led to a decomposition of the dye after only 14 days. Therefore new oxazine dyes were synthesized at CCS [30] and tested for their application in the NO_2-sensitive membrane. In addition, the influence of the matrix was taken into account and various polymers and plasticizers were screened in order to extend the lifetime [24]. Currently a novel approach to measuring NO_2 optically is being evaluated in cooperation with S.M.

Fig. 7. One of the prescribed test fires: smoldering combustion of beech wood. When the fire stopped, the NO_2-concentration was 140 ppb.

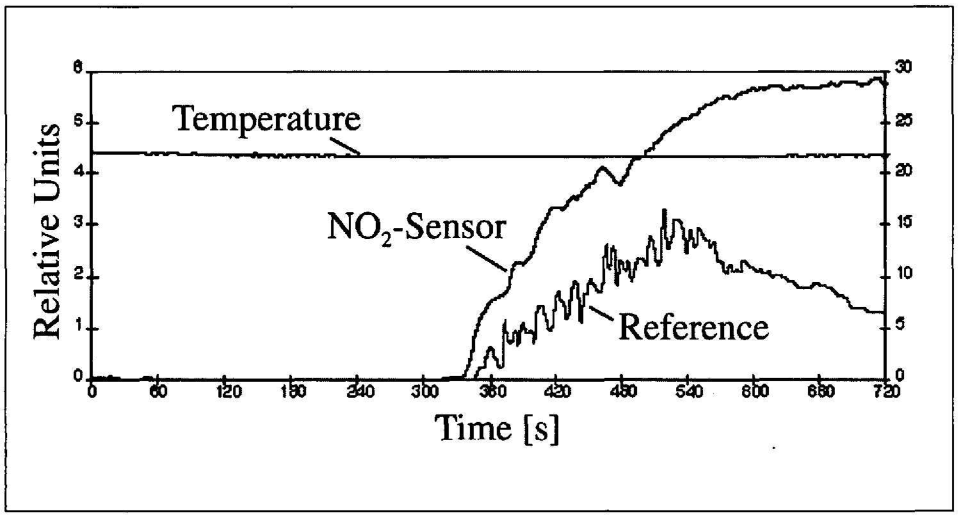

Fig. 8. Measurements made during the smoldering combustion of beech wood with the NO_2-sensor, an optical smoke density measurement device (MIREX EC-911, Delta, DK) and a temperature sensor.

Zakeeruddin (group of M. Graetzel, EPFL). The focus is on incorporating metal phthalocyanines into polymer layers.

The NH_3-sensitive membrane has been stable since the first experiments began in 1997 and therefore clearly fulfils the requirements for longevity. Therefore we are convinced that in the near future we will be able to equip fire detectors with a gas sensor array which detects gases like NO_2, NH_3, CO_2 and CO.

3. Conclusions

The fire detector introduced by Bosch Telecom containing the NO_2-sensitive membrane developed at CCS has many advantages over conventional fire detectors. The main aim to reduce the number of false alarms can be fulfilled with the NO_2-selective sensor. Additionally, the recognition time could, in some cases, be decreased, depending on the burning material. From the scientific point of view, a new way of detecting gases with polymeric membranes has been launched.

4. Methods

4.1. *Chemicals and Reagents*

The NO_2-selective membrane (polymer layer) incorporates 0.5 to 10 weight% of a Co(III)-cobyrinate complex (aquacyanocobalt (III)-hepta(2-phenylethyl) cobyrinate perchlorate, nitrite-ionophore I (Fluka Chemie AG, Buchs) or PEFA 10105, which works as a selective host compound. The nitrite ionophore I was resynthesized and modified (PEFA 10105) by Pentapharm AG, Basel. ETH 5418 ([11-[(1-butylpentyl)oxy]-11-oxoundecyl-4-{[9-(dimethylamino)-5*H*-benzo[a]phenoxazine-5-ylidene]amino}-benzenate]) was usually used in a concentration of 50 to 200 mol% relative to the complexing agent. Poly(vinylchloride) (PVC) and DOS (bis(2-ethylhexyl) sebacate) as plasticizer (Fluka Chemie AG, Buchs) were used as the matrix.

4.2. *Sensor Coating*

At CCS the membranes were obtained using a stainless steel capillary (Hamilton Bonaduz AG) connected to the valve of a dosimeter (Microlab 500, Hamilton Deutschland GmbH, Darmstadt, D). The membrane components were dissolved in freshly distilled cyclopentanone. 0.2 µl of this solution was injected onto the photodiode of the optical chip. After the evaporation of the solvent, the resulting layers were between 8–25 µm thick depending on the viscosity of the polymer mixture. The reproducibility of the coating was around 90% [31].

4.3. *Measurement Setup*

A measurement setup to test gas sensors under various conditions was built at CCS. Dry synthetic air (quality 5.5, Sauerstoffwerk Lenzburg AG) was split in two lines before two mass flow controllers (MKS Instruments Deutschland GmbH, München, D). One branch was humidified by guiding the air over the water surface in a 2-neck glass flask, thus avoiding the formation of water droplets. A relative humidity of up to 93% could be obtained. This was monitored with a hygrometer (Rotronic, Bassersdorf) located after the measurement cell. These two lines of synthetic air were merged to provide the desired carrier gas stream, which additional lines could be connected to. Mass flow controllers diluted 10 ppm NO_2 balanced in synthetic air (Carbagas, Rümlang) together with the interfering gases, which were mixed with the carrier gas stream to produce a gas flow in a variable range of 20–400 ml/min with 0.005 ppb to 3 ppm NO_2. Stainless steel or Teflon tubing was used throughout. A program based on LabView 5.1 was especially designed to operate the whole system and to collect and analyze the sensor data. A data acquisition (DAQ) multifunction card (Lab-PC-1200 from National Instruments, Ennetbaden) was used to connect an IBM PC 330 to self-made electronic control modules for the mass flow controllers and for the sensor chip.

The LED of the optical chip was driven with a sinus-modulated direct current at 10 kHz. Thus, the responses of the photodiodes, which were illuminated through the polymer membranes, had the same frequency. These signals were amplified and filtered with bandpass filters before passing to the DAQ card. Finally, the corresponding amplitudes were obtained from these alternating signals using a fast Fourier transformation implemented in the LabView program. With this self-developed module we were able to increase the signal–noise ratio by up to one order of magnitude compared with an LED operating in constant current mode [31].

To characterize the sensor responses to a fast exchange of gases, *e.g.* to enable kinetic measurements, a flow-through cell was designed with minimal volume and a constant cross-section along the flow-channel [13]. This meant that no flow dependency was observed and the real-time interaction of the polymer membrane with the gas sample could be investigated.

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