Semiconductor gas sensor for detecting NO and CO traces in ambient air of road traffic

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Abstract

The present article describes sensor elements that have been made by means of thick-film and thin-film techniques. By choosing the sensor materials and the operating temperature, these sensor elements can be selective for carbon monoxide (CO) and nitric dioxide (NO_2). In addition, the time-response behaviour of these sensors has been measured and optimized for application in a motor vehicle (return-air control/air conditioning).

1. Introduction

Gas sensors based on resistive changes of selected semiconductor materials have been successfully used for many years for simple monitoring functions in households and in industry. Metallic oxides are generally applied as base materials; due to their surface properties they are very suitable for the detection of noxious gases. Metallic-oxide gas sensors using tin dioxide as the base material are mainly suited for inflammable gases (hydrocarbons), hydrogen sulfide (H_2S) and carbon monoxide (CO). Because of the sensor element's operating temperature (150–550 °C), partial selection for certain gases and gas groups can be realized and also improved further by including catalytic additives (e.g., platinum). Depending on whether the gas to be analysed is oxidizing or reducing, either a resistance increase or a resistance decrease will be obtained. The manufacturing technology for these commercial sensor elements is sintering (manual technique).

Pollutants, such as nitric oxides (NO), hydrocarbons (HC) and CO, are emitted by all motor vehicles (passenger cars, buses, trucks, motorcycles) in more or less high concentrations. By using catalysts in the exhaust system of passenger cars, their emission is markedly reduced but not entirely eliminated. In particular, utility vehicles (trucks and buses) having diesel engines still emit a large number of chemical reaction products. True, when comparing this emission gas with that of Otto carburettor engines it is classified as low-emission gas due to its low CO content, but the emission of soot, nitric oxides and aromatic hydrocarbons, which can also be recognized as a 'smoke streamer', still represents a substantial problem.

Since even small concentrations of this kind of exhaust gas are perceived by the human sense of smell as disturbing and disagreeable, legal regulations have already been imposed to reduce pollutant emission. Since reducing all pollutants may still take several decades, additional protection measures against these gases in traffic would be desirable.

In the past, conditioning systems equipped with activated carbon filters were already presented to eliminate the disturbing pollutants from the ambient air in passenger vehicles [1]. However, for reasons of cost these systems were not widely used. But already nowadays sensor systems are used in certain vehicles to provide active protection of the passengers against pollutants. To this end, a gas sensor at the radiator box near the engine permanently measures the pollutant content (carbon monoxide) of the outside air. If a predefined alarm value is exceeded, the ventilating system's flaps will automatically be closed for a specified time. These measures can eliminate short-term loads occurring in front of traffic lights, in underground garages or in tunnels.

Figure 1 shows the time dependence of this pollutant peak. It clearly represents the correlation between the pollutant concentration outside the vehicle at measuring point 3 and the pollutant concentration inside the passenger cabin (measuring point 1). A time shift within

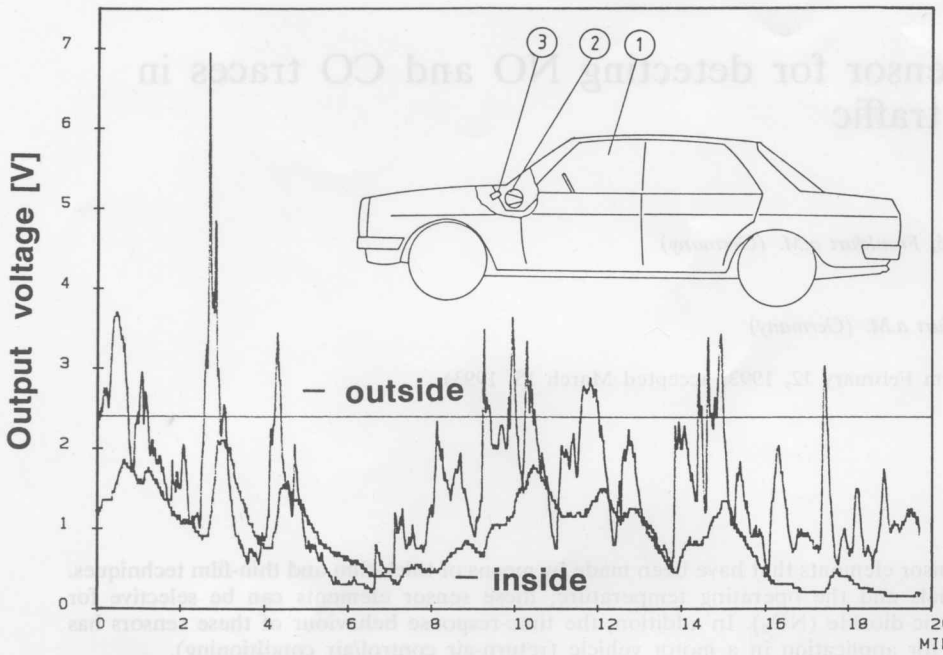


Fig. 1. Measurement of the pollutant concentration (carbon monoxide) outside and inside a vehicle (output voltage of sensor electronics vs. time): (1) measuring point of the sensor for measurement within the cabin; (2) ventilator; (3) measuring point of the sensor for air measurement outside.

the range of a few seconds can be recognized between the two concentration curves. This time shift of concentration peaks can be attributed to the delays in the air-conditioning system and those in the memory effect inside the passenger cabin. Figure 1 also shows that early detection of the pollutant peak and subsequent response (closing of flap) can prevent a build up of pollutant concentration inside the passenger cabin.

These values are permanently collected and evaluated by a microprocessor unit. Since the predefined alarm value cannot be optimal for any imaginable environmental situation, the alarm value is permanently calculated anew on the basis of the available measured values and adapted to real environmental conditions. The alarm value is ascertained from a fixed portion and a variable portion by taking the mean of all measured values over a specified time interval (5 min). Figure 2 shows a typical signal pattern for taking the average and thus also performing the alarm value calculation.

Variable threshold

$$= \text{solid threshold} + [X(\text{avr.}) - X(\text{min.})/S] \qquad (1)$$

with X(avr.) = mean value over 150 single measurements in a time interval of 5 min, X(min) = minimum measured value within the time interval and S = 'empirical quotient' ($\approx$ 3–4).

Since sensors available at present [2] are mainly sensitive to CO, the exhaust gases of trucks and buses can only be detected inadequately.

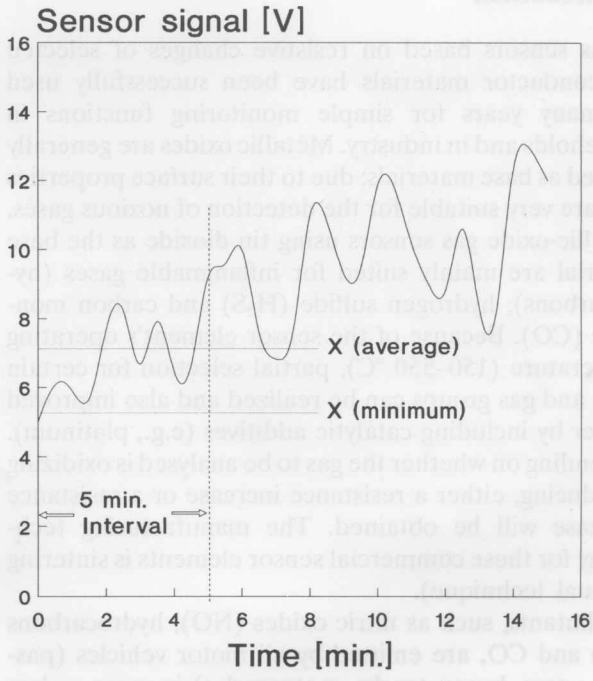


Fig. 2. Typical signal curve of a sensor, with the definitions for taking the mean and limit-value calculations.

Therefore the starting points for further development of this return-air system should mainly be found in sensor element development in order to be able to implement a selective measurement of carbon monoxide

and nitric dioxide in a real gas mixture. For nitric dioxide measurement in particular, no reliable sensor elements providing a sufficient response speed for this application exist. True, sensors based on phthalocyanine [3, 4] show a very good sensitivity to nitric oxides in the sub-ppm range but have a bad response speed of about a minute. The present authors have already described a sensor element that seems suitable for this kind of application [5, 6].

2. Sensor structure

A hybrid structure was used for the sensor element, which mainly consisted of an electrode/heater structure in thin-film technique and a gas-sensitive thick-film structure [7]. Due to lack of space, the thin-film technique was used for the interdigital electrode arrangement, since at structure widths below 100 μm there are natural limits to the thick-film technique. Hence the substrate surface of 5 mm × 5 mm could be reduced. As gas-sensitive layers, tin dioxide was used for CO measurement and indium tin oxide for NO_2 measurement. The advantage of the thick-film structure is that the porous layer structure is of better long-term stability and easier to make [8] with regard to manufacturing techniques than a thin-film structure. Moreover, a thin-film structure does not provide any advantages with regard to the response speed like the ones presumed by several authors in previous work.

The sensor element's optimal operating temperature is different for each component. It was revealed that the optimal substrate temperature for CO measurement (tin dioxide) is 450 °C, whereas NO_2 measurement is optimal at 300 °C. Figure 3 shows the temperature

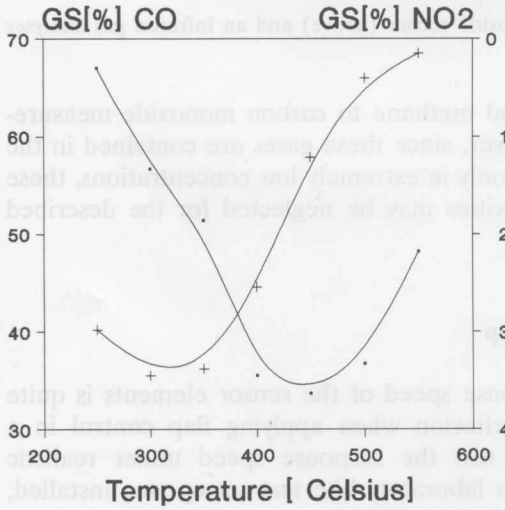


Fig. 3. Gas sensitivity of the tin dioxide sensor for different substrate temperatures: ■, 1000 ppm CO; +, 80 ppm NO_2.

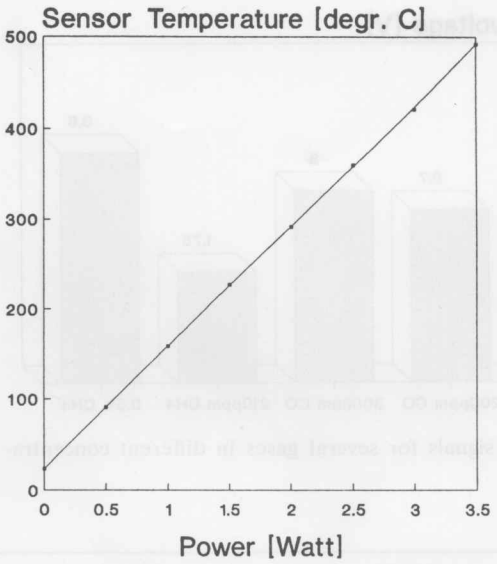


Fig. 4. Power input of the sensor with a substrate surface of 25 mm^2.

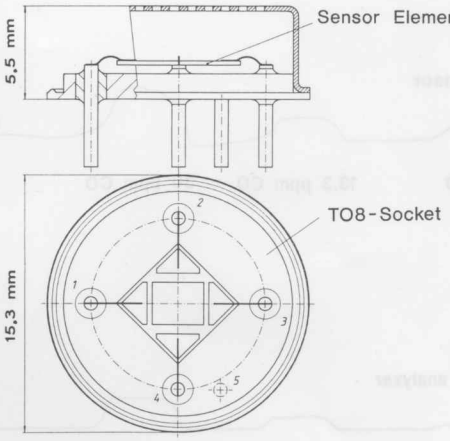


Fig. 5. Cross section (upper part) and view (below) of the sensor structure.

dependence of gas sensitivity (GS) for the tin dioxide sensor. In this case GS is indicated as

$$GS = R(\text{gas})/R(\text{air}) \times 100\% \qquad (2)$$

with R(gas) = resistance with the test gas and R(air) = resistance in pure air.

The necessary electric load is represented in Fig. 4 as a function of the substrate temperature. Correspondingly, NO_2 measurement (300 °C) requires a power ≈2 W whereas CO measurement (450 °C) requires ≈3 W. For laboratory and driving tests the sensor element was integrated in a standard case (TO8 base) (Fig. 5). The gas passes to the active sensor element through boreholes in the cover cap and sets off a reaction with chemisorbed oxygen on the sensor's surface. This reaction sets free electrons in the semicon-

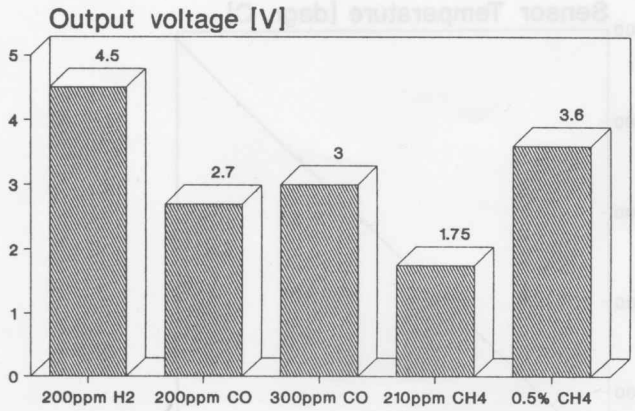


Fig. 6. Output signals for several gases in different concentrations.

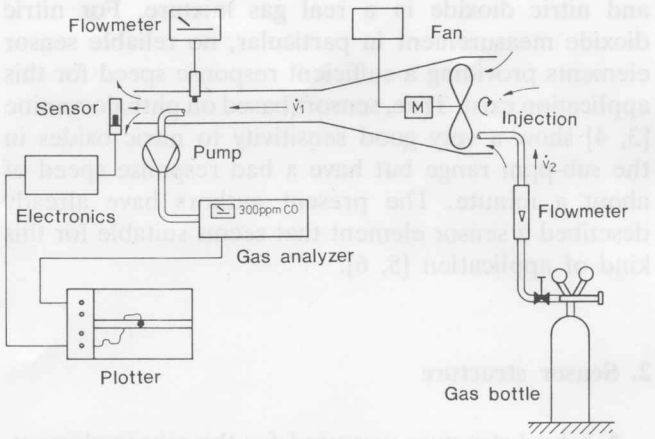


Fig. 7. Test device for measuring the response behaviour in real conditions.

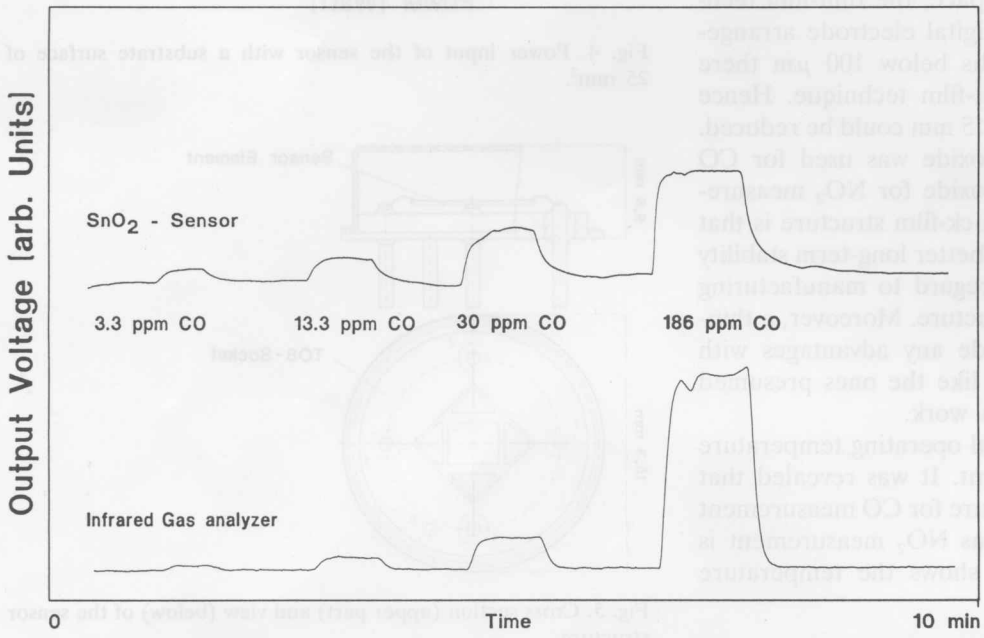


Fig. 8. Measuring signals with different gas concentrations, recorded with a tin dioxide sensor (above) and an infrared gas analyser (below) as a reference measurement in the test devices.

ductor material, which will then lead to a resistance reduction [9].

The selectivity between the two sensor elements can be taken from Fig. 3. Thanks to the different substrate temperatures, the selectivity between the sensors can be increased considerably. Especially in the case of transient signal patterns, additional effects result from different response speeds. It turned out that the response behaviour also depends on the substrate temperature and thus produces an additional effect in the event of non-steady gas changes (peaks).

Besides, these sensors also exhibit cross sensitivity to other gases, which may be important for the described application. Figure 6 shows the cross sensitivity of hydrogen and methane to carbon monoxide measurement. However, since these gases are contained in the ambient air only in extremely low concentrations, these cross sensitivities may be neglected for the described application.

3. Test set-up

The response speed of the sensor elements is quite a decisive criterion when applying flap control in a vehicle. To test the response speed under realistic conditions, a laboratory-like test set-up was installed, by means of which these tests could be performed. The set-up, as shown in Fig. 7, essentially consists of

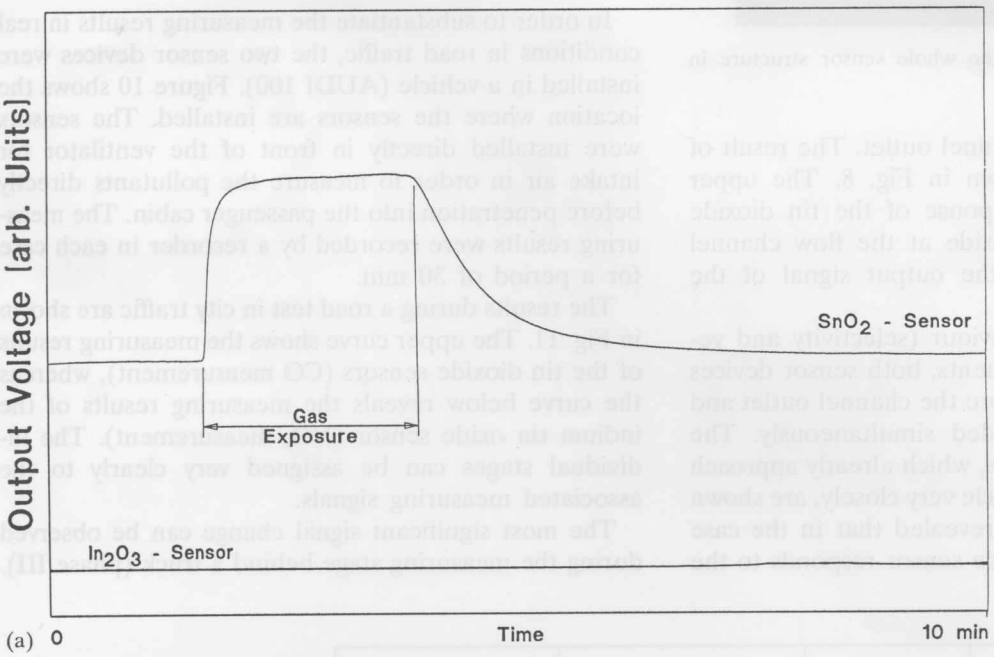
a flow channel in which a controllable flow is produced by means of a fan. The flow in the channel was permanently checked with a flowmeter and recorded. Then the complete sensor device was fixed to the flow channel's outlet so that direct flow against the sensor was ensured. To produce the corresponding pollutant peaks in the flow channel, CO and NO_2, respectively, were added by dosing from a gas cylinder in the concentration range 100–1000 vpm to the aspirated ambient air. By diluting with ambient air a pollutant peak of the corresponding concentration was then attained. The concentration could be calculated from the dilution as follows:

Peak concentration

$$= V2/(V1+V2) \times \text{test gas concentration} \qquad (3)$$

with $V1$ = volume flow in flow channel, $V2$ = volume flow of test gas and $V1 \gg V2$.

For a check, the current gas concentration was simultaneously measured with an infrared gas analyser (type BINOS 1, Leybold-Heraeus GmbH, Germany)



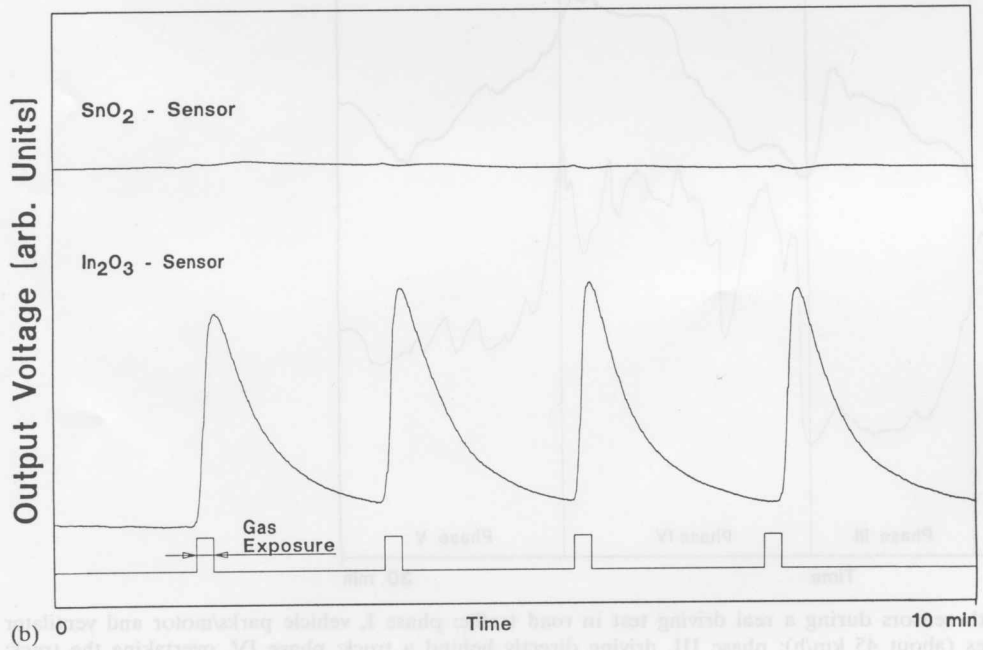


Fig. 9. Injection of about (a) 1000 vpm CO and (b) 100 vpm NO_2 into the stream channel and in a dilution ratio of 1:10.

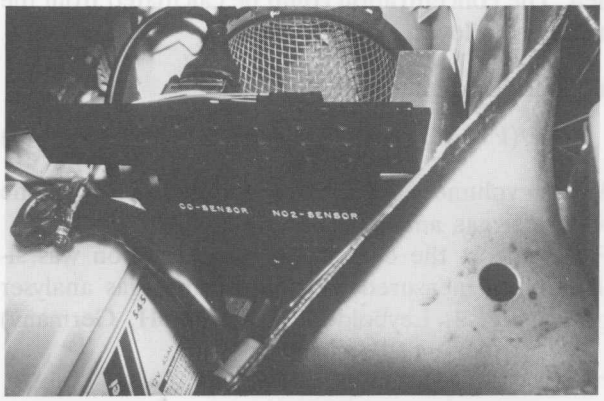


Fig. 10. Installation location of the whole sensor structure in front of the fresh-air blower.

and sampling at the flow channel outlet. The result of such a measurement is shown in Fig. 8. The upper part represents the step response of the tin dioxide gas sensor for carbon monoxide at the flow channel outlet in comparison with the output signal of the infrared gas analyser.

To test the response behaviour (selectivity and velocity) of the two sensor elements, both sensor devices were installed in parallel before the channel outlet and the measuring results recorded simultaneously. The results of these measurements, which already approach real conditions inside the vehicle very closely, are shown in Fig. 9(a) and (b). It was revealed that in the case of CO injection the tin dioxide sensor responds to the peak very quickly and sensitively, whereas the indium tin oxide sensor (lower line) does not detect the peak. In the reverse case the indium tin oxide sensor very quickly and sensitively indicates a NO_2 pollutant peak, whereas the tin dioxide sensor only shows slight signal changes. From this result an extremely high selectivity can be derived for the measurement of carbon monoxide and nitric dioxide in the ambient air.

4. Driving tests

In order to substantiate the measuring results in real conditions in road traffic, the two sensor devices were installed in a vehicle (AUDI 100). Figure 10 shows the location where the sensors are installed. The sensors were installed directly in front of the ventilator for intake air in order to measure the pollutants directly before penetration into the passenger cabin. The measuring results were recorded by a recorder in each case for a period of 30 min.

The results during a road test in city traffic are shown in Fig. 11. The upper curve shows the measuring results of the tin dioxide sensors (CO measurement), whereas the curve below reveals the measuring results of the indium tin oxide sensor (NO_x measurement). The individual stages can be assigned very clearly to the associated measuring signals.

The most significant signal change can be observed during the measuring stage behind a truck (phase III).

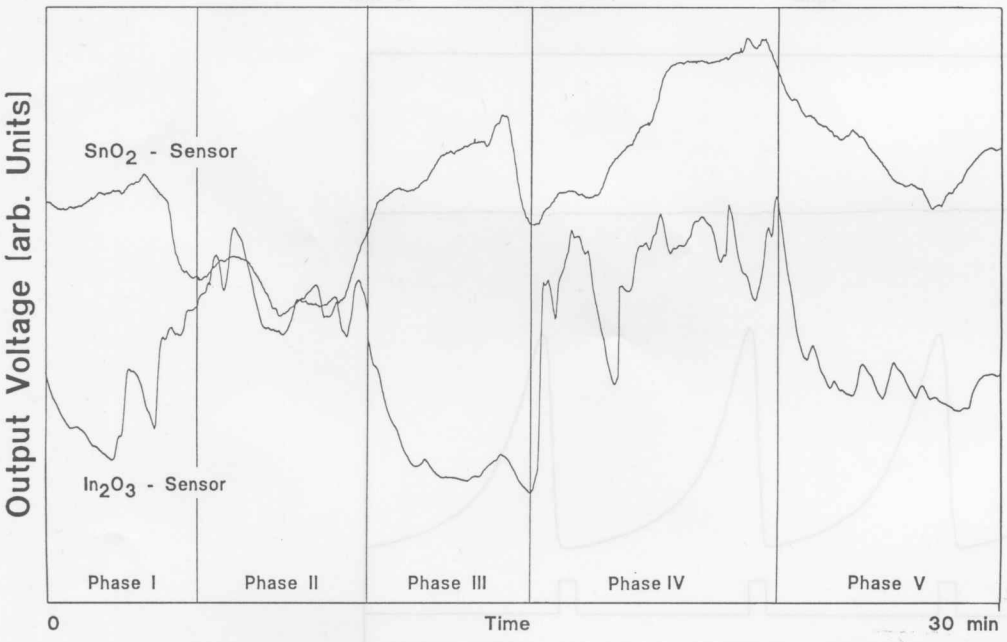


Fig. 11. Response behaviour of both sensors during a real driving test in road traffic: phase I, vehicle parks/motor and ventilator are running; phase II, vehicle drives (about 45 km/h); phase III, driving directly behind a truck; phase IV, overtaking the truck; phase V, driving within a wooded area.

Due to the high nitrogen oxide content of the truck exhaust gas, the indium tin oxide sensor reacts with an immediate resistance drop. After overtaking, the resistance value returns immediately to the original initial value.

As neither the ventilator within the vehicle nor the substrate temperature of the sensor was controlled, additional disturbance effects on the sensor signals occurred. These effects are due to changes of temperature of the sensor element caused by the non-controlled ventilator flow. This effect can be observed particularly when switching over from phase 1 (parking) to phase 2 (driving). However, this fault can be completely compensated by additional temperature control of the sensor element, thus rendering a reliable measurement within the vehicle realistic.

The whole sensor structure was tested in the vehicle for a period of about one year, and no significant change of the sensor properties was observed.

Besides the very rough environmental conditions, such as temperature, vibrations/shock, the sensor devices were, of course, also submitted to influences from chemical substances, such as gasoline vapour, liquid detergents for windscreens (ethanol) and liquid detergents for car washing (undefined). However, the sensor remained undamaged.

5. Conclusions

Semiconductor gas sensors based on tin dioxide and indium tin oxide have been tested for their use in a vehicle for climatic control. The test revealed that both the response speed of these hybrid sensors and the selectivity for carbon monoxide and nitrogen dioxide are sufficient.

These results were impressively substantiated in a driving test in real conditions in road traffic. However, additional efforts still have to be made for a mass-produced design of these sensors. In particular, the temperature stability of the uncontrolled sensor substrate still needs improvement.

The heating power can be adapted to the respective environmental conditions by an additional temperature measurement on the chip. this permitting the achievement of a stable output signal.

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Biographies

Gerhard Wiegleb (1956) was born in Recklinghausen, Germany. In 1980 he received his diploma in applied physics at the University of Essen, Germany. Till 1990 he worked in the R&D departments on analytical instruments and sensors and on automotive sensors and actuators in various companies in Germany. In 1990 he received his Dr. rer. nat. degree from the University of Witten-Herdecke, Germany, and since then he has been R&D manager of the department on analytical instruments and chemical sensors for process-control and environmental monitoring at Hartmann&Braun AG in Frankfurt/M.

Joachim Heitbaum (1940) received his diploma in physics and his Dr. rer. nat. degree (electrochemistry) at the University in Bonn in 1970 and 1972, respectively. After further research work at universities in Bonn and in Cleveland, USA (Professor E. Yeager), he was appointed professor at the University in Bonn in 1981 and full professor for physical chemistry at the University of Witten-Herdecke in 1985. In 1989 he joined Chemetall GmbH in Frankfurt/M, where he heads R&D activities in surface technology.