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Micro Hot Plate-Based Sensor Array System for the Detection of Environmentally Relevant Gases

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A monolithic stand-alone gas sensor system is presented, which includes on a single chip an array of three metal oxide-coated micro hot plates with integrated MOS-transistor heaters, as well as a specifically designed digital system architecture. An octagonal-shaped micro hot plate design with MOS-transistor heaters has been adopted for the three gas sensors. The integrated circuitry includes a programmable digital temperature regulation, digital sensor readout units, and a standard serial interface. The programmable digital temperature controllers enable individual regulation of the micro hot plate temperatures in constant or dynamic mode. Nanocrystalline tin oxide thick films with different Pd dopings (undoped, 0.2 and 3 wt %) were used. Gas test measurements for environmentally relevant gases were carried out and evidenced detection limits of less than 1 ppm for carbon monoxide, or 100 ppm for methane, both at 40% relative humidity. Temperature modulation techniques were successfully applied for improved analyte discrimination.

There is a strong interest in micro hot plate-based gas sensors due to miniaturization advantages such as low power consumption and the possibility of applying new dynamic sensor operation modes as a consequence of the low thermal mass of such hot plates.[1−4] The sensitive materials that are commonly used with such hot plates include metal oxides such as tin dioxide that show large resistance changes at elevated temperatures (200−400 °C) upon gas exposure and exhibit high sensitivities to environmentally relevant gases such as CO, CH_4, or NO_2.

A well-known problem of tin dioxide, however, is its lack of selectivity. This problem is usually dealt with by using an array of sensors in combination with multicomponent or pattern recognition algorithms such as principal component regression, partial least squares (PLS), multiway analysis, or artificial neural networks.[5,6] The use of different catalytic additives (noble metals such as Pt, Pd) to the tin dioxide also changes its sensitivity to the various gaseous analytes.[7] Another parameter that can be varied is the operation temperature so that an array of micro hot plates with individually controlled temperatures, the hot plates of which are covered with different sensitive materials, expands the overall information that can be extracted from metal oxide-based gas sensor systems.[8,9]

The advantage of chemical microsensors in complementary metal oxide semiconductor (CMOS) technology is that the sensor and circuitry can be combined on a single chip. Gas and biochemical sensors realized as monolithic CMOS-integrated systems feature a high degree of miniaturization, a broad variety of possibilities to integrate additional functions, and favorable signal-to-noise characteristics because signal amplification and conditioning can be done on the spot, where the signal is generated. The high initial electronics design and integration efforts pay off, particularly for sensor arrays, since the integrated electronics can be shared between the different sensors and since the sensor readout and control can be handled via a common integrated interface.[10−12]

The fabrication of single micro hot plates and sensor systems in CMOS technology has been demonstrated previously.[13,14] One approach included the use of different metal oxide materials on a single large hot plate featuring different sectors.[15] In another approach, several micro hot plates with addressing circuitry and a differential amplifier for sensor readout were combined on a single chip.[16] A first array of micro hot plates with integrated analog temperature controllers was reported on in ref 17.

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(1) Simon, I.; Bârsan, N.; Bauer, M.; Weimar, U. *Sens. Actuators* **2001**, *B73*, 1−26.
(2) Semancik, S.; Cavicchi, R. E.; Wheeler, M. C.; Tiffany, J. E.; Poirier, G. E.; Walton, R. M.; Suehle, J. S.; Panchapakesan, B.; DeVoe, D. L. *Sens. Actuators* **2001**, *B77*, 579−591.
(3) Savage, N. O.; Roberson, S.; Gillen, G.; Tarlov, M. J.; Semancik, S. *Anal. Chem.* **2003**, *75*, 4360−4367.
(4) Weiller, B. H.; Fuqua, P. D.; Osborn, J. V. *J. Electrochem. Soc.* **2004**, *151* (3), H59−H65.
(5) Gutierrez-Osuna, R. *IEEE Sens. J.* **2002**, *2*, 189−202.
(6) Hines, E. L.; Boilot, P.; Gardner, J. W.; Gongora, M. A. Pattern Analysis for Electronic Noses. In *Handbook of Machine Olfaction*; Pearce, T. C., Schiffman, S. S., Nagle, H. T., Gardner, J. W., Eds.; Wiley-VCH: Weinheim, Germany, 2003; pp 133−160.
(7) Kappler, J. Bârsan, N.; Weimar, U.; Dieguez, A.; Alay, J. L.; Romano-Rodriguez, A.; Morante, J. R.; Göpel, W. *Fresenius J. Anal. Chem.* **1998**, *361*, 110−114.
(8) Stankova, M.; Ivanova, P.; Llobet, E.; Brezmesa, a. J.; Vilanovaa, X.; Gràcia, I.; Cané, C.; Hubalekc, J.; Malyszc, K.; Correiga, X. *Sens. Actuators* **2004**, *B103*, 23−30.
(9) Lee, D.-S. Huh, J.-S.; Lee, D.-D. *Sens. Actuators* **2003**, *B93*, 1−6.
(10) Hagleitner, C.; Hierlemann, A.; Lange, D.; Kummer, A.; Kerness, N.; Brand, O.; Baltes, H. *Nature* **2001**, *414*, 293−296.
(11) Vancura, C.; Rüegg, M.; Li, Y.; Hagleitner, C.; Hierlemann, A. *Anal. Chem.* **2005**, *77*, 2690−2699.
(12) Hierlemann, A.; Baltes, H. *Analyst* **2003***, 128*, 15−28.
(13) Graf, M.; Barrettino, D.; Zimmermann, M.; Hagleitner, C.; Hierlemann, A.; Baltes, H.; Hahn, S.; Bârsan, N.; Weimar, U. *IEEE Sens. J.* **2004**, *4*, 9−16.
(14) Graf, M.; Barrettino, D.; Taschini, S.; Hagleitner, C.; Hierlemann, A.; Baltes, H. *Anal. Chem.* **2004**, *76*, 4437−4445.
(15) Wöllenstein, J.; Plaza, J. A.; Cané, C.; Min, Y.; Böttner, H.; Tuller, H. L. *Sens. Actuators* **2003**, *B 93*, 350−355.
(16) Afridi, M. Y.; Suehle, J. S.; Zaghloul, M. E.; Berning, D. W.; Hefner, A. R.; Cavicchi, R. E.; Semancik, S.; Montgomery, C. B.; Taylor, C. J. *IEEE Sens. J.* **2002**, *2*, 644−655.

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All these devices are based on resistive heating elements. An alternative heating scheme is a transistor-type heater. A key advantage of transistor-based heaters is the reduction of the overall power consumption of the sensor systems, since no power transistor is needed to drive the heating current. The heat dissipated by such a power transistor can be used to directly heat the hot plates, which leads to a considerable reduction in power consumption. Transistor heater-based devices have been proposed and realized in SOI−CMOS technology[18] and also in conventional CMOS technology by applying dedicated post-CMOS micromachining steps.[21]

In this paper, a device is presented, which features three micro hot plates that have been monolithically integrated with digital temperature controllers, readout, and interface circuitry. The micro hot plates are heated by means of MOS transistors and are covered with drop-deposited nanocrystalline tin dioxide (different noble metal additives) as sensitive layer. All sensor parameters and values can be set and read out via a digital interface, which drastically reduces the packaging efforts since the number of bond connections of the array is the same as for a single micro hot plate. Full advantage of the features offered by applying CMOS technology is taken, and a stand-alone sensor system has been developed, since only a communication interface to a computer is necessary for operation. This interface, e.g., a universal serial bus (USB) interface, provides, at the same time, all needed lines for the sensor control and readout and the power supply (5 V), so that the system can be run directly from the USB port of a computer or laptop by means of, e.g., LABVIEW software. The system exhibits one of the highest levels of integration of miniaturized gas sensor systems so far. Microtechnological aspects of this system have already been presented at relevant conferences[19,20] so that the emphasis of this paper is on the chemical sensor applications of this system and the possibilities that the system offers to potential users.

SYSTEM DESCRIPTION

Sensor System Architecture. The equivalent-circuit representation and components of a micro hot plate are shown in Figure 1. The two different heating schemes, heating resistor and heating transistor, are displayed. In the case of the heating transistor, the source drain current that can be adjusted via the gate voltage is used to heat the hot plate structure so that a transistor with a very wide gate region has to be used, in our case, an octagonal transistor located along the edges of the heated area (Figure 2). Most micro hot plates and monolithic sensor systems published to date include resistive heating elements as it was pointed out in the introduction. Driving a resistive heater on chip requires a power transistor (Figure 1A). A voltage drop across this transistor occurs, and a massive fraction (up to 20−30%) of the consumed power is dissipated on the chip, which does not contribute to heating the membrane. Industrial CMOS processes offer the advantage of using active heating elements by, for example, realizing a metal oxide semiconductor (MOS) transistor-type heater on the membrane. The power transistor for driving the resistive heater is no longer necessary, and all heat development takes place directly on the membrane and contributes to the micro hot plate heating (Figure 1B). The working range for conventional MOS transistors, however, is between −40 and 120 °C. This is much lower than the target operating temperature of 200−350 °C of the hot plates so that the transistor, in most cases, loses its transistor characteristics. It was recently shown that the characteristic functionality of the transistor can be preserved even at such high temperatures if the transistor is placed on an electrically isolated micromachined structure suspended by a dielectric membrane.[21] This implies that the silicon plate, in which the source and drain regions are embedded, has no electrical contact to the chip substrate. Further advantages of the transistor heating scheme include the possibility to apply new heater control modes (direct digital control) and the fact that the full supply voltage range can be applied to the heater. A low-pass filter to avoid extreme current peaks and fluctuations in the heater structure extends the heater lifetime.

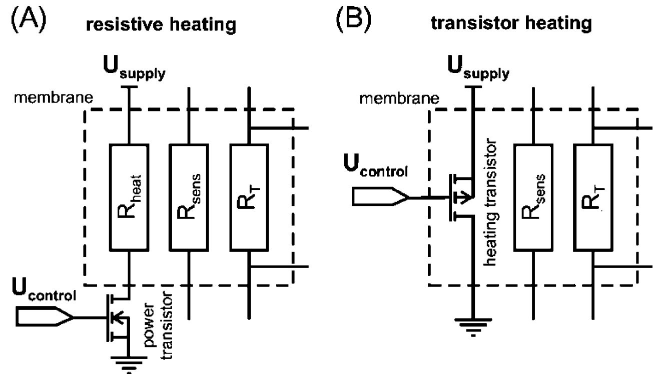

Figure 1. Different micro hot plate heating schemes: (A) resistive heater with power transistor and (B) MOS transistor heater. R_{heat} denotes the heating resistor, R_{sens} the metal oxide sensor resistance, and R_T the temperature sensor resistance.

All three hot plates in the presented sensor system feature such transistor heaters. Figure 2 shows a simplified diagram of the most important system architecture blocks, emphasizing the system modularity. Each micro hot plate features a polysilicon resistor as temperature sensor, a MOS transistor heater, and the tin dioxide-based chemiresistor. The voltage drop across the temperature sensor is converted by an analog-to-digital (A/D) converter into a digital signal. The converted signal serves as input to the digital proportional integral derivative (PID) temperature controller so that the temperature control loop is closed. The three independent controllers provide individual temperature regulation for each hot plate. The MOS heating transistors are driven in pulse density modulation. The converters and a multiplier are circuitry parts that consume most of the chip area. For this reason, they have been realized only once and are accessed in a time-sharing mode. The control unit takes care of scheduling the different operations and of controlling the access of all hot plates to the shared multiplier and A/D converter.

For each hot plate, an individual bias current is generated and applied to the tin dioxide-covered platinum electrodes. The voltage

(17) Barrettino, D.; Graf, M.; Song, W. H.; Kirstein, K.-U.; Hierlemann, A.; Baltes, H. *IEEE J. Solid-State Circuits* **2004**, *39*, 1202−1207.

(18) Udrea, F.; Gardner, J. W.; Setiadi, D.; Covington, J. A.; Dogaru, T.; Lu, C. C.; Milne, W. I. *Sens. Actuators* **2001**, *B78*, 180−190.

(19) Graf, M.; Taschini, S.; Käser, P.; Hagleitner, C.; Hierlemann, A.; Baltes, H. *Proc. IEEE MEMS Conf.,* Maastricht, The Netherlands, 2004; pp 351−354.

(20) Graf, M.; Frey, U.; Reichel, P.; Taschini, S.; Barsan, N.; Weimar, U.; Hierlemann, A. *Proc. IEEE Sens. Conf.*, Vienna, Austria, 2004; pp 776−779.

(21) Graf, M.; Müller, S. K.; Barrettino, D.; Hierlemann, A. *IEEE Elect. Dev. Lett.* **2005**, *26*, 295−297.

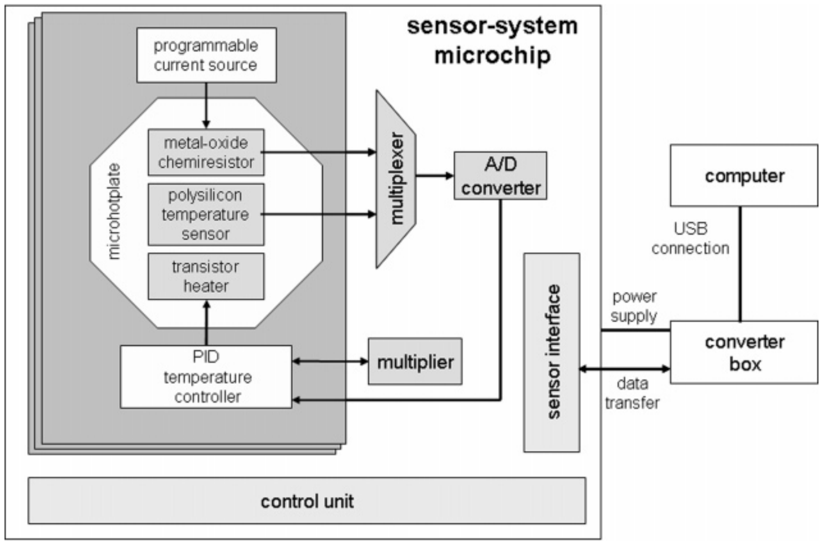

Figure 2. Block diagram of the sensor system including a computer and converter box for data transfer and power supply.

drop across the resistive material is then converted to a digital value with the same A/D converter that is also used for the temperature control loop. The bias currents can be individually adjusted with a 10-bit value over a range from 0.1 to 90 μA. Therefore, the resistance of the SnO_2 material that can vary over orders of magnitude (from a few hundred ohms to 10 MΩ, depending on the addition of noble metal catalyst) can be measured with sufficient accuracy of $\sim\pm0.05\%$ (min. 10 Ω) of the actual resistance value. All parameters, such as target temperature, bias currents, PID coefficients, and some control flags are stored within the control unit and are accessed via a standard inter-integrated circuit (I^2C) interface.[22] The details of the circuitry implementation will be described elsewhere.[23]

The chip is a stand-alone microsensor system that does not need any external measurement equipment for sensor control and readout. The sensor system chip has been connected to a computer via an I^2C-to-USB converter box (Figure 2); i.e., in this box is a microcontroller that translates the I^2C format coming from the chip into USB format for the computer or laptop. The power supply of the chip is also provided by the USB connection. The sensor can also be read out directly by a microcontroller and is, therefore, well suited for handheld devices or distributed sensor networks.

Micro Hot Plate and Transistor Heater. A schematic cross section of the micro hot plate is shown in Figure 3A. A polysilicon resistor is used to measure the temperature on the heated area of the micro hot plate. The resistance change upon gas exposure of the nanocrystalline thick-film SnO_2 layer is read out with the help of two noble metal-coated electrodes. To ensure a good thermal insulation, only the dielectric layers of the industrial CMOS process form the membrane. The inner section of the membrane additionally includes a n-well silicon island underneath the dielectric layers. The n-well is electrically isolated and serves as a heat spreader. It also hosts the PMOS transistor serving as heating element. Owing to the efficient electrical decoupling of the n-well island silicon from the bulk silicon of the chip, the transistor preserves transistor characteristics even at high temperatures. Moreover, the excellent thermal isolation allows for achieving high temperatures in the heated area, whereas the temperature on the bulk chip only marginally increases (2−3 °C above ambient temperature) A close-up of the membrane is shown in Figure 3B. The heating transistor features 5-μm gate length and 720-μm overall gate width. A special ring-shaped transistor arrangement was chosen, which leaves enough space in the center for the resistive temperature sensors and the sensor electrodes. Two temperature sensors realized as identical polysilicon thermistors and exhibiting a nominal resistance of 10 kΩ are integrated in the heated area. The temperature sensor in the lower part of the heated area is connected to the control circuitry, whereas the sensor in the upper part is not connected to circuitry. This second sensor can be used for an accurate calibration of the membrane temperature and for the verification of the controller performance. The total size of the membrane is 500 by 500 μm^2 (Figure 3B). The octagonal shape of the n-well silicon island provides a relatively long distance between the heated membrane area and the cold bulk chip. Thus, the heat dissipation via metal connections is considerably reduced. The overall membrane layout is highly symmetric to ensure a homogeneous temperature and stress distribution.

FABRICATION

The chip is fabricated in industrial 0.8-μm CMOS technology.[24] The total chip dimensions are 5.5×4.5 mm^2. To establish a good contact to the sensitive layer, the electrodes are first covered with 50-nm Ti/W (diffusion barrier and adhesion layer) and, then, with a 100-nm Pt layer, which is patterned by lift off. The membranes are released by etching the wafer from the backside with 6 M KOH at 90 °C. An electrochemical etch-stop technique is used to preserve the central n-well islands, which host the heating

(22) I^2C (inter integrated circuit, inter-IC) is a communication standard developed by Philips, Eindhoven, The Netherlands: http://www.semiconductors.philips.com/buses/i2c/facts.

(23) Frey, U.; Graf, M.; Taschini, S.; Kirstein, K.-U.; Hierlemann, A. *IEEE J. Solid-State Circuits*, submitted.

(24) 0.8 μm CMOS technology as provided by austriamicrosystems, Unterpremstätten, Austria, www.austriamicrosystems.com.

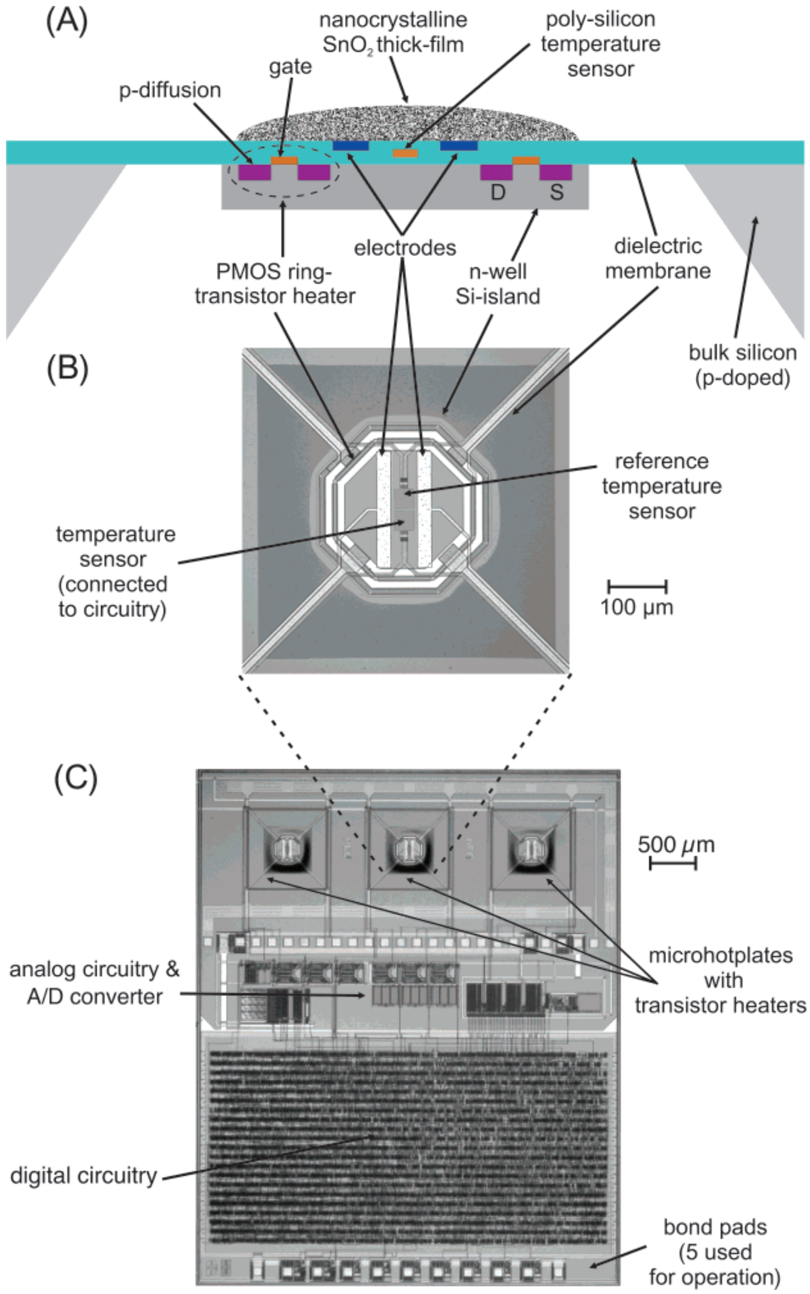

Figure 3. (A) Schematic cross section of the micro hot plate with PMOS transistor heater, (B) close-up of the heated area, (C) chip micrograph showing the micro hot plate array and the associated circuitry. See also ref 19.

transistors.[25] The deposition and subsequent annealing of the nanocrystalline tin dioxide at 400 °C conclude the postprocessing sequence, which is fully CMOS-compatible.[14,17,26] The micro hot plates have been coated with three different nanocrystalline thick-film sensing materials. The first membrane is covered with a Pd-doped SnO_2 layer (0.2 wt % Pd), a layer optimized for CO detection. The sensitive layer on the second contains 3 wt % Pd, which renders this material more sensitive to CH_4. The third micro hot plate has an undoped SnO_2-sensitive layer, which is expected to be most sensitive to NO_2. The materials were provided and deposited by means of drop-coating by the company AppliedSensor, Reutlingen, Germany.[27]

Figure 3C shows the fabricated chip featuring a trisectional floor plan with digital circuitry at the bottom, which includes the temperature controller and the interface, little analog circuitry (A/D and D/A converter of the temperature sensors) in the center, and the three micro hot plates at the top.

Figure 4 shows a packaged sensor chip and the packaging concept. A commercially available standard TO-8 socket with 16 pins has been chosen.[14] Only five connections (bonds) are needed for the sensor system operation. The chips are affixed with the die-attach Epotek H72, which is electrically nonconductive. To

(25) Müller, T.; Brandl, M.; Brand, O.; Baltes, H. *Sens. Actuators* **2000**, *A84*, 126−133.

(26) Briand, D.; Krauss, A.; van der Schoot, B.; Weimar, U.; Bârsan, N.; Göpel, W.; de Rooij, N. F. *Sens. Actuators* **1997**, *68*, 223−233.

(27) AppliedSensor GmbH, Reutlingen, Germany, www.appliedsensor.com.

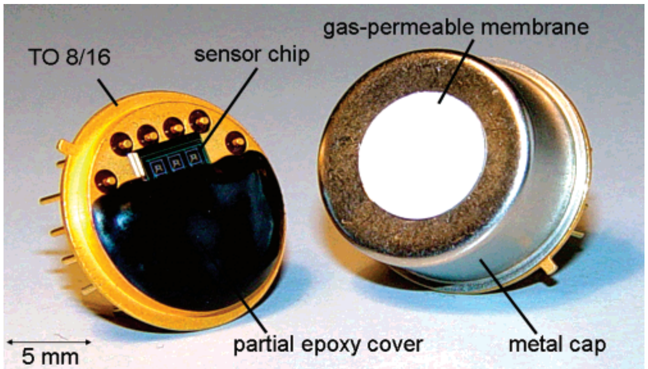

Figure 4. Photo of a packaged sensor system chip. See also ref 19. The partial epoxy cover enables free analyte access to the sensors. The metal cap with gas-permeable membrane provides mechanical and dust protection.

protect the bond wires and the circuitry, the chip is partially covered with a glob top epoxy. A metal cap with a gas-permeable membrane is mounted on top of the TO socket for protection. The array chip is thus well protected against dust and mechanical impact. The cap allows also for integration of metal sieves and filters, which is an important feature for tuning the selectivity of the sensor system.

EXPERIMENTAL SECTION

Sensor System Setup. The fully packaged chip is connected via the USB-to-I^{2}C converter box to a laptop or palmtop computer (Figure 2). A LABVIEW program was implemented as user-friendly interface for setting the sensor system parameters, for generating the individual temperature profiles for the hot plates, and to display the measurement results.[23] Any arbitrary waveform can be generated to modulate the temperature on the hot plates (dynamic or static operation). The software translates the digital sensor system output into micro hot plate temperatures and sensor resistance values. A second-order polynomial has been used for temperature calculation. The calibration procedure for the temperature sensors has been described elsewhere.[13]

Gas Manifold. Vapors were generated from gas bottles with calibrated target gas concentrations (e.g., CO) and then diluted as desired using computer-driven mass-flow controllers and synthetic air (oxygen/nitrogen mixture without humidity) as carrier gas. The different humidity contents were generated by passing a fraction of the overall gas stream through a water bubbler, which was kept at a defined temperature. All vapors were mixed and temperature-stabilized before entering the thermoregulated test chamber (30 °C). For more details on the manifold, see ref 13 and 14.

RESULTS

Temperature Control. The performance of the temperature controller was measured in the tracking mode. Figure 5 shows a graph, where the temperature of one of the three micro hot plates is kept at a constant temperature of 300 °C, the temperature of the second micro hot plate is modulated using a sine wave of 10 mHz, while to the third micro hot plate regtangular temperature steps of 150, 200, 250, 300, and 350 °C are applied. Temperature measurements on one hot plate operated at a constant temperature in the stabilization mode showed a variance below 1 °C, even though the temperature of the neighboring hot plates was, during the same time, dynamically modulated (sine wave, ramp, steps). This is a consequence of the individual hot plate temperature control, without which thermal cross talk between the hot plates would be clearly detectable. The power dissipation of the chip is ~190 mW when all three hot plates are simultaneously heated to 350 °C.

Gas Test Measurements. Several chemical test measurements have been conducted with the array chip. Figure 6 shows the results that have been obtained simultaneously from three micro hot plates coated with different tin dioxide-based materials at operation temperatures of 280 and 330 °C in humidified air (40% relative humidity at 22 °C). The first micro hot plate (μHP1) is covered with a Pd-doped SnO_2 layer (0.2 wt % Pd), which is optimized for CO detection, whereas the sensitive layer on micro hot plate 3 contains 3 wt % Pd, which renders this material more responsive to CH_4. The material on micro hot plate 2 is pure tin oxide, which is known to be sensitive to NO_2 .[20] Therefore, the electrodes on micro hot plate 2 of do not measure any significant response upon exposure to CO or methane. The baseline resistance of micro hot plate 1 is ~47 kΩ, that of hot plate 2 is

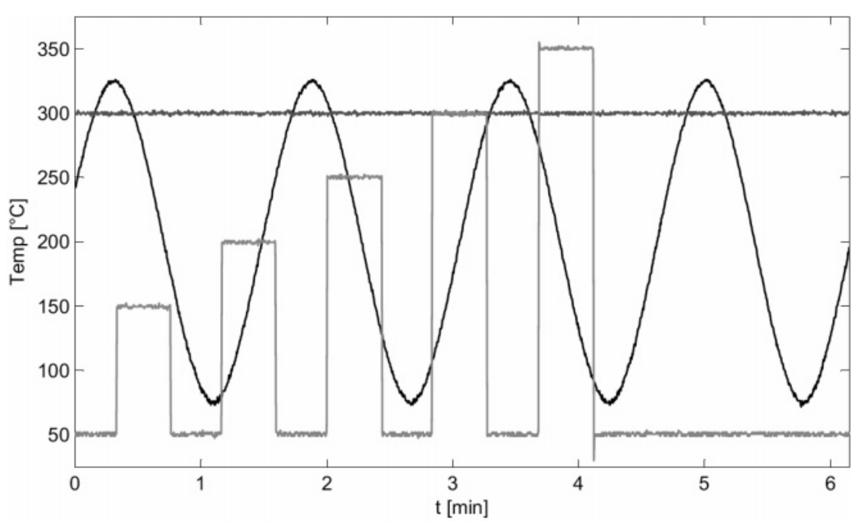

Figure 5. Temperature tracking in PID control mode. One hot plate is kept at constant temperature; the temperature of the second micro hot plate is modulated in a sinusoidal way. Rectangular temperature steps are applied to the third micro hot plate.

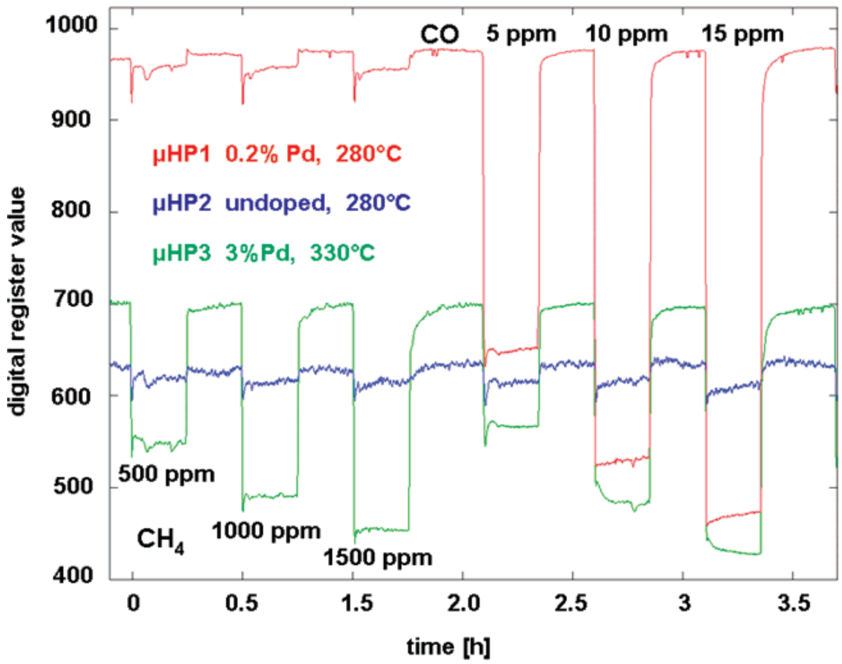

Figure 6. Sensor response of the three microhotplates (μHPs) with different sensitive layers (undoped tin dioxide, 0.2% weight Pd, and 3% weight Pd), and operated at different temperatures (280° to 330 °C) upon exposure to CO and CH_4 at 40% r.h. The raw sensor signals represented as digital register values are displayed.

370 kΩ, and the material on hot plate 3 features a rather large resistance of nearly 1 MΩ.

As is evident from Figure 6, the responses of the three sensitive materials to the test gases CO and CH_4 are very different. The lightly Pd-doped (0.2%) tin dioxide shows large responses to CO, and very small responses to CH_4, whereas the heavily Pd-doped (3%) tin dioxide exhibits comparably smaller responses to CO, but also responds to hydrocarbons, as in this case, methane. The pure tin dioxide shows hardly any response to CO or methane but has been measured to provide large signals upon exposure to nitrogen dioxide at concentrations as low as 10 ppb.[20]

The two test gases were simultaneously detected with detection limits of less than 1 ppm for CO and less than 100 ppm for CH_4. The array of micro hot plates with individually controlled temperatures, the hot plates of which are covered with different sensitive materials, drastically augments the overall information that can be extracted from such sensors and, then, can be used as input for suitable data deconvolution tools (multicomponent analysis, pattern recognition).[5,6] This is particularly important in detecting analytes in the presence of interferences or in analyzing mixtures.

Figure 7A shows measurements using the sensor system with each hot plate being operated at a preset constant temperature over a period of 19 h. The baseline drift on the order of 5% has been removed for this representation. The respective gas concentrations have been applied during 20 min alternated with periods of purging with pure air (also 20 min). In the first measurement series, CO has been dosed at concentrations of 1, 2, 5, and 10 ppm. The next series consist of mixtures of CO and CH_4. Methane concentrations of 100, 200, 500, and 1000 ppm were added to CO as it is displayed in Figure 7B.

Figure 7B shows the true concentrations as applied in the gas manifold and the prediction values resulting from a PLS regression on the data after precedent calibration. The input to the PLS regression consisted of the difference values between equilibrium signal during gas exposure and baseline signal. To cope with the nonlinearity of the data, the quadratic term of the zeroth-order coefficient was added to the input as described in ref 28. A leave-one-out cross validation using Haaland's criterion revealed that the optimum prediction can be achieved using five factors resulting in standard errors of prediction of 0.8 ppm for CO and 105 ppm for CH_4. The predictions resulting from the model validation are shown as gray bars in Figure 7B. As the standard error of prediction suggests, the predictions correspond very well to the true concentrations.

In a second measurement series, the temperature of the hot plates was modulated as shown in Figure 8. Each gas exposure cycle of a total of 30 min was followed by 30-min purging with pure air. The sequence of one cycle (Figure 8a) included first keeping the hot plates at room temperature for 11 min and then setting the temperature during 3 min to 350 °C followed by another 3 min at room temperature. Then the actual measurement follows, which is a 3-min ramp from room temperature (25 °C) to 350 °C and which is repeated twice as shown in Figure 8A. Closeups of the sensor responses to various gas compositions as recorded during the last 2.5 min of the temperature ramp (from approximately 100 to 350 °C, indicated as gray shading in Figure 8A) are shown in Figure 8B. The relative resistance changes with regard to the baseline resistance are plotted versus time, with one measurement lasting 2.5 min. The sensor response of the pure tin dioxide, plotted as a dashed line, does not show any significant signal change or response, as this sensor is predominantly sensitive to NO_2 but neither to carbon monoxide nor to methane. The other two materials show distinct signal changes and response trends whether exposed to methane or to carbon

(28) Mitrovics, J.; Weimar, U.; Göpel, W. Linearisation in Multicomponent Analysis Based on a Hybrid Sensor-array with 19 Sensor Elements. *Technol. Digest Transducers*; Stockholm, Sweden, 1995; Vol. 1, pp 707–710.

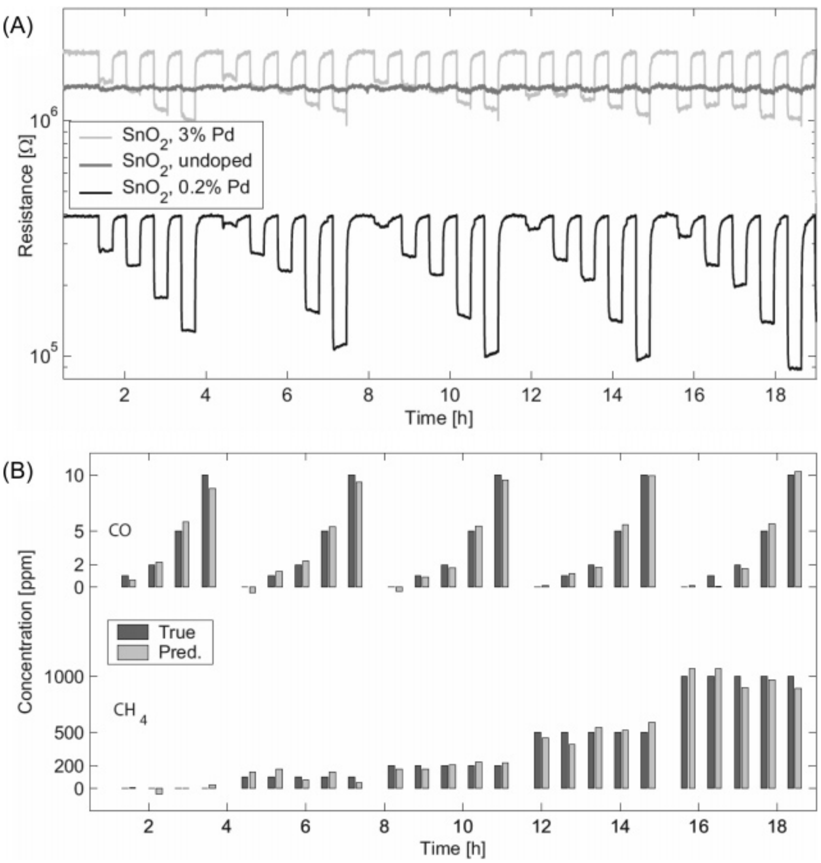

Figure 7. Sensor measurements of different concentrations of CO and CH_4, including mixtures, at 20% relative humidity. All sensors were operated at constant temperature. (A) Responses of three differently doped tin dioxide-based sensors after baseline drift correction. (B) True gas concentrations as adjusted in the gas manifold and predicted concentrations resulting from the application of a multicomponent algorithm to the sensor data (PLS).

monoxide. Methane causes the response of the heavily doped sensor, plotted as a solid line, to exhibit a local resistance maximum and a subsequent resistance decrease toward the end of the temperature ramp so that methane is usually measured at higher operation temperatures (above 300 °C) since the methane-induced resistance changes, and consequently, the sensor sensitivity is most pronounced at higher temperatures The response shape of the lightly doped tin dioxide-coated sensors does not perceivably change. The effects of carbon monoxide exposure are more drastic. The resistance values of both heavily and lightly Pd-doped sensor materials significantly drop and tend to increase a bit toward higher temperatures (end of the ramp), a behavior that is more pronounced for the heavily doped material. The curvature of the signal versus time or temperature plots also decreases. Carbon monoxide can be detected best at rather low operation temperatures around 250−280 °C. For simultaneous exposure to methane and carbon monoxide, finally, a superposition of the features evoked by the single gases can be observed. Again, we see the resistance maximum of the heavily doped sensor toward the end of the temperature ramp. Figure 8 hence evidences that dynamic signals as provided by applying temperature modulation can be used for analyte discrimination and qualification, a finding that has been published also by other groups.[29−33]

The relevance of these results in the context of this paper is that the presented system enables the fully programmable simultaneous application of any arbitrary temperature profile to three different sensor materials so that a multitude of sensing conditions or "virtual sensors" can be generated within a very short time. The developed system hence can be used for many applications and analytes, and the system parameters can be adjusted according to the detection problem at hand.

CONCLUSION

A monolithic gas sensor system is presented, which, for the first time, includes on a single chip a complete array of three micromachined metal oxide-coated micro hot plates with integrated transistor heaters, as well as specifically designed analog and digital circuitry. The micro hot plates are covered with semiconducting metal oxides that have to be operated at elevated temperatures up to 400 °C and change their resistance upon gas exposure. The integrated circuitry is realized in CMOS technology and includes a programmable temperature regulation, digital sensor readout units, and a standard serial interface. The system has been designed as a stand-alone gas sensor system so that only a standard interface to a computer is necessary for operation (power supply and communication).

A multitude of sensing conditions or "virtual sensors" can be generated by arbitrary temperature modulation on the three hot

(29) Heilig, A.; Bârsan, N.; Weimar, U.; Göpel, W. *Sens. Actuators* **1997**, *B43*, 45−51.
(30) Lee, A. P.; B. Reedy, J. *Sens. Actuators* **1999**, *B60*, 35−42.
(31) Ionescu, R. Llobet, E.; Vilanova, X.; Brezmes, J.; Sueiras, J. E.; Calderer, J.; Correig, X. *Analyst* **2002**, *127*, 1237−1246.
(32) Nakata, S.; Hashimoto, T.; Okunishi, H. *Analyst* **2002**, *127*, 1642−1648.
(33) Gutierrez-Osuna, R.; Gutierrez-Galvez A, A.; Powar, N. *Sens. Actuators* **2003**, *B93*, 57−66.

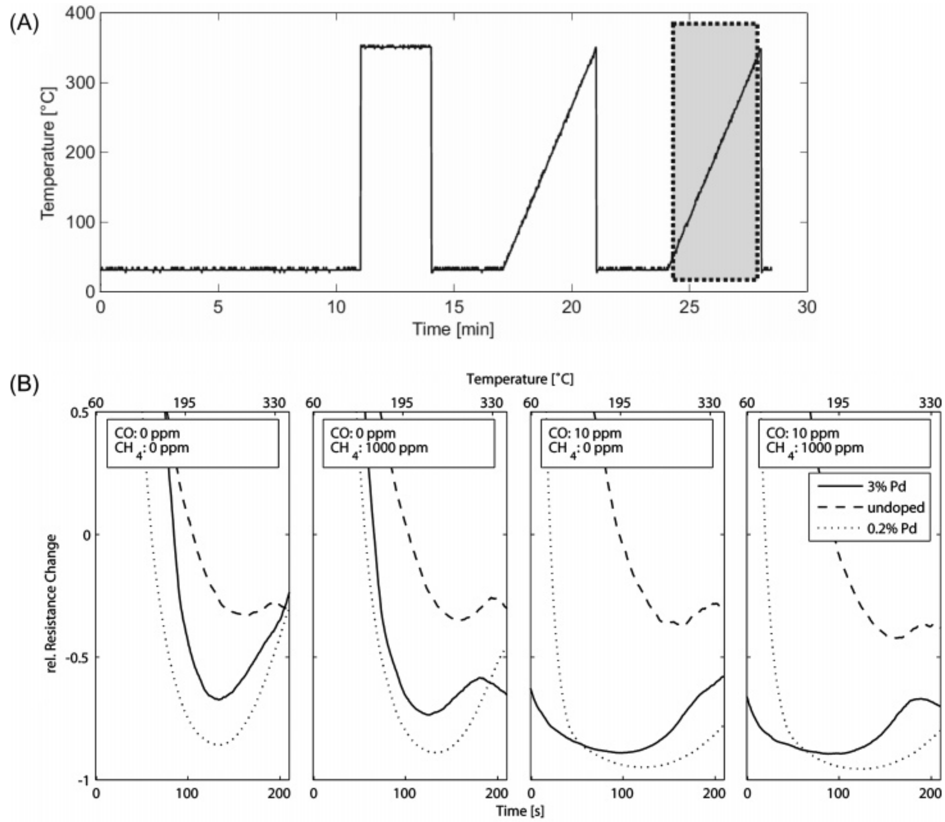

Figure 8. (A) Temperature profile as used to perform the temperature-modulated measurements. The sensor responses to the different gases as recorded during a temperature ramp (shaded part, 100−350 °C) are shown in (B). The sensor responses are plotted as relative resistance changes with respect to the initial baseline resistance ($(R - R_0)/R_0$).

plates so that the system is capable of simultaneously monitoring several target gases. The system may serve a wide variety of applications such as gas hazard and leakage detection in household and industrial settings and indoor air quality monitoring in automobile applications, and it may be used as a personal safety device or in conjunction with traffic guidance systems to monitor and regulate local air pollution. Moreover, the three-hot-plate system can be used for material research such as differential scanning calorimetry.[17] The system provides a defined temperature ramp to the hot plate hosting the material under investigation while the current flowing through the heating transistor is monitored. This way phase transitions can be detected by strong changes in the heating currents.

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