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Integration of MOX gas sensors on polyimide hotplates

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Abstract

In this communication, we report on the integration of metal-oxide gas sensors on polymeric micro-hotplates made on polyimide and silicon substrates. Low-power consumption micro-hotplates with platinum electrodes and heaters were fabricated on polyimide membranes. Their thermal behavior was optimized using temperature probing at the micro-scale level coupled with thermal simulations. Tin oxide thick films were successfully integrated on these polyimide micro-hotplates using the drop coating technique. The annealing process of the tin oxide drops on the polyimide substrate was investigated and gas measurements are presented. Compared to the polyimide hotplates on silicon substrates, the hotplates made on polyimide sheets are simpler to process and more robust, and therefore, they are more suitable for the integration of metal-oxide films. Finally, a wafer level packaging technique using multiple polyimide layers was developed and led to a polymeric platform for metal oxide sensors. The technology is also promising for the integration of polyimide humidity sensors, of resistive and capacitive gas-sensitive polymeric films to realise fully flexible gas sensor arrays.

Keywords: Metal-oxide (MOX); Gas sensors; Polyimide hotplates; Plastic gas sensors; Polymeric gas sensors; Wafer level packaging

1. Introduction

Fully plastic gas sensors, meaning sensitive layers and transducers made out of polymers, can have some advantages over conventional silicon or ceramic technology. Their simplified processing and increased flexibility would allow new applications, such as their integration in textiles, wraps and in RFID tags. The state of the art in that field is mostly limited to the use of polymeric films as gas-sensitive layers on inorganic substrates. However, polymeric sensors based on the organic electronics technology and more recently the combination of polymeric gas sensitive films on polymeric transducers are raising more and more interest in the scientific community [1–3]. In this communication, we present the validation of the compatibility of metal-oxide gas sensitive films with low-power polymeric transducers. The development of transducers on polymers for metal-oxide gas sensors has been reported lately, nevertheless, the complete integration of metal-oxide (MOX) films on polymeric hotplates has not been demonstrated yet [4,5]. Neither the compatibility of the deposition and the annealing process of MOX films nor the gas sensing performances of such devices have been addressed and evaluated so far.

Compared to the work we have recently reported on the development of micro-heating elements on polyimide (PI) for sensors and actuators [5], we detail here the application of polymeric hotplates for the realisation of low-power metal-oxide gas sensors. Specific fabrication processes are evaluated for the integration of metal-oxide gas sensors on two types of PI hotplates, made on PI sheets and on silicon substrates. The compatibility of the annealing process of the MOX films was investigated, and the thermal behavior and the gas sensing performances of the devices were addressed. The annealing treatment of PI hotplates coated with tin oxide was established. Gas measurements were performed and the integration of MOX gas sensors on low-power polymeric transducers was demonstrated. The use of PI sheets as substrate was identified as the most promising technology for the integration of gas sensitive MOX films. A wafer level packaging (WLP) process based on UV patternable PI films spin coated on a PI sheet capped with a polymeric filtering membrane has been developed. The WLP process proposed brings the technology a step further towards the realisation of polymeric and flexible gas sensing devices.

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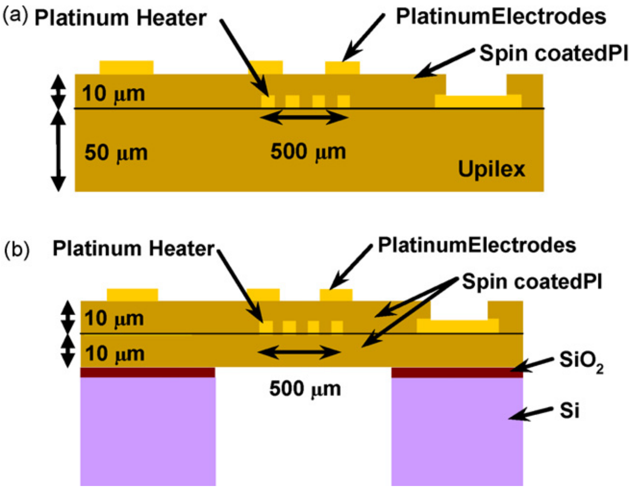

Fig. 1. Designs of the gas sensors realised (a) on polyimide sheets and (b) on silicon substrates.

2. Experimental

2.1. Design

The transducers consist of low-power micro-hotplates made of PI coated with interdigited metallic electrodes. Two different types of transducers were evaluated; one type was made on PI sheets (Upilex-S, T_g at 500 °C) while the other one was made on silicon substrates using only photosensitive polyimide (PI 2731 from HD MicroSystems, $T_g > 350$ °C), see Fig. 1. The heater is embedded in between two PI layers with the electrodes patterned on top of the device.

The wafer level packaging concept is presented in Fig. 2. The proof of concept was realised on sensors integrated on the Upilex PI sheet. At the wafer level, a 35 µm-thick rim was made around each sensor active area from PI. The whole PI wafer was drop coated with MOX. A 50 µm-thick gas permeable membrane came on top of the PI frame to seal the sensors at the wafer level.

2.2. Fabrication

The processing was simple for the devices realised on PI sheets. 50 µm-thick wafers with a diameter of 100 mm were cut in a sheet of Upilex-S. The 150 nm-thick Pt/Cr e-beam evaporated heaters were patterned using lift-off. A 9 µm-thick photosensitive PI film (PI 2731 from HD MicroSystems) was added on top of the Pt heater to electrically isolate it from the electrodes. Before curing the polymer was exposed to UV light and developed to pattern windows to access the heater contact pads. The curing of the PI involved temperature ramps from room temperature to a plateau at 375 °C (30 min) that made the PI stable at 450 °C. 150 nm-thick platinum electrodes were then patterned on top of the spin coated PI by lift-off.

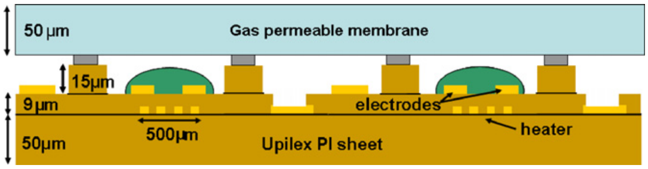

Fig. 2. Schematic drawing of the cross-section of wafer level packaging concept.

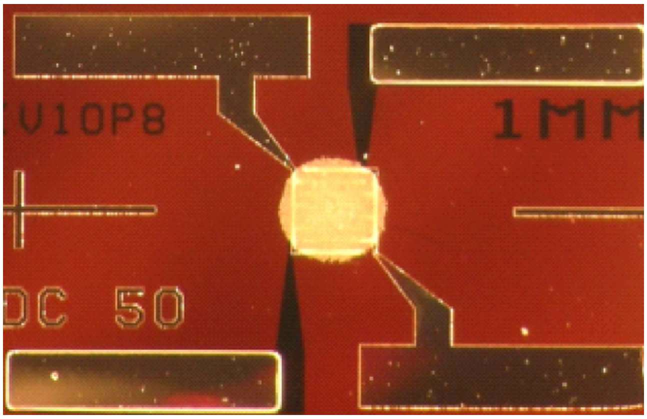

Fig. 3. Complete metal-oxide gas sensors on a polyimide micro-hotplate made on a polyimide sheet as substrate.

For the hotplates made on silicon, a 300 nm-thick oxide film was thermally grown on a 100 mm wide, 390 µm-thick double side polish silicon wafer. The PI 2731 was spun over the oxide film and cured, using the same process as described above, to form a 9 µm-thick film to be used as membrane. The 0.2 nm-thick Pt heater and the 150 nm-thick electrodes were patterned using a lift-off process with another 9 µm-thick photosensitive PI layer spun and cured in between. The polyimide membrane was released using deep reactive ion etching of silicon with the oxide film acting as an etch-stop. The oxide was removed in buffered hydrofluoric acid (BHF).

The polyimide micro-hotplates on Upilex and on silicon withstood an annealing in air at a maximum temperature of 450 °C, the membrane from the silicon device exhibited a significant membrane deformation compared to the Upilex device [5]. Therefore, these polymeric gas-sensing platforms were drop coated with SnO_2 and annealed in air at 450 °C. The MOX gas sensors realised on the two types of polyimide micro-hotplates are presented in Figs. 3 and 4.

At the wafer level on sensors made on PI sheet, a 35 µm-thick rim was made around the active area of each device by adding

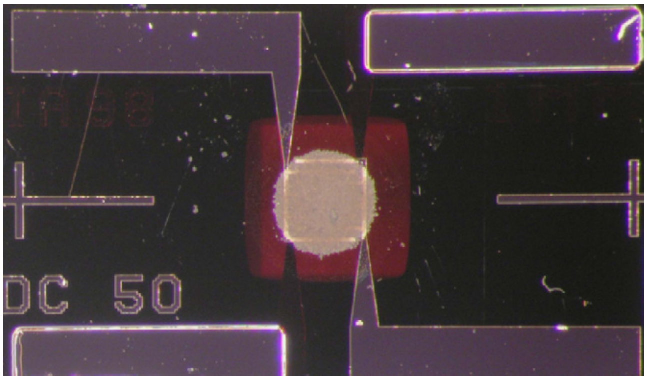

Fig. 4. Complete metal-oxide gas sensors on polyimide micro-hotplate made on a silicon substrate.

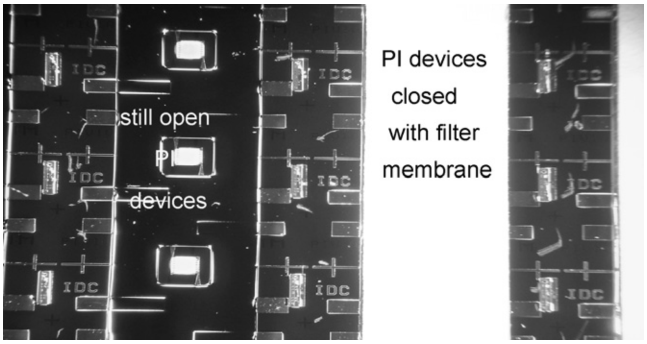

Fig. 5. WLP of metal-oxide gas sensors made on a polyimide sheet with a column of sensors covered with the filtering membrane.

on top an extra layer of spun photosensitive PI, which was cured using the process described above. After coating and annealing of the drop sensitive films, the devices could be packaged at the wafer level (WLP) by sealing them with a thin gas permeable membrane attached to the PI rim all over the wafer, as shown in Fig. 5, simplifying the approach previously published for such sensors made on silicon nitride micro-hotplates [8,9]. Finally sensors could be separated in individual encapsulated chips.

2.3. Packaging

The devices were packaged before performing the characterisation of their thermal and gas sensing properties. The PI sensors on silicon were packaged using a standard procedure for such devices; they were glued (Epotek 70E) on TO-5 headers and wire bonded. The PI sensors on Upilex sheet were also fixed on TO-5 headers but with a plastic rim acting as a spacer in between the sensor on PI and the TO socket. A hole was drilled in the plastic spacer to form a plastic rim around the active area of the device to ensure a good thermal insulation of the PI hotplate from the TO socket. As for the PI sensors on silicon, a Epoxy glue was used to fix all these parts together and electrical connections were made using wire bonding.

2.4. Characterisation and optimization of the thermal characteristics

The temperature versus power calibration of the PI microhotplates was performed using miniaturized thermocouples. The thermocouple probes are obtained by welding two S type Wollaston wires (Pt and Pt-10%Rh), with a diameter of 1.3 µm [6]. By coupling the temperature distribution on a PI hotplate measured using a micro-thermocouple with thermal simulations performed in CoventorWare, the thermal conductivity, k_{PI}, of the spin coated PI was determined and used to improve the heater geometry in a second run of complete transducers with electrodes. Temperature measurements were performed on a simplified micro-hotplate made of 1.5 mm-wide and 9 µm-thick PI membrane with a platinum heater on top operated at 66 mW, corresponding to a temperature of 325 °C, which is typical for the operation of tin oxide gas sensors. The hotplate is illustrated in Fig. 6. Thermal simulations of the PI membrane only with a power of 66 mW dissipated by Joule heating in the heater were performed in CoventorWare. The temperature measured on the silicon rim at the edge of the membrane was set as the boundary condition on the sides of the membrane and air convection was set on top and underneath the membrane [6,7]. The convection coefficient of about 140 $\mathrm{W\,m^{-2}\,K^{-1}}$ was defined related to our previous work performed on similar micro-hotplates geometry and the value of the thermal conductivity k_{PI} in $\mathrm{W\,m^{-1}\,K^{-1}}$ was adjusted to have a match between the maximum temperature reached in the simulation and the temperature profile obtained with the experimental temperature measurements performed at this power [6].

2.5. Gas measurements

Gas measurements were performed at 325 °C under different concentrations of CO (20, 50 ppm), NO_x (0.35, 1.7 ppm), and CH_4 (700, 5000 ppm) in air. PI sensors on Upilex sheet and on silicon have been measured at a gas mixing station with a total flow of 200 ml at 50% Rh. Moreover, a reference sensor based on drop coated tin oxide gas sensors made on standard silicon was included [10]. As carrier gas, zero grade air was used. Each test gas pulse lasted approx. 10–50 min, depending on the type of gas tested, and was followed by a carrier gas pulse to stabilize the signal back at the base line.

3. Results and discussion

3.1. Electrical and mechanical characteristics

The electrical resistance of the Pt/Cr heaters of the hotplates made on the PI sheets were of 200 Ω. The resistance value of the Pt/Cr heater was modified, going up by a factor of 14% in average, during the annealing of the tin oxide coating at 450 °C, due to the diffusion of Cr in Pt. However, compared to Pt alone, the use of Cr improved the adhesion of the Pt films on PI as

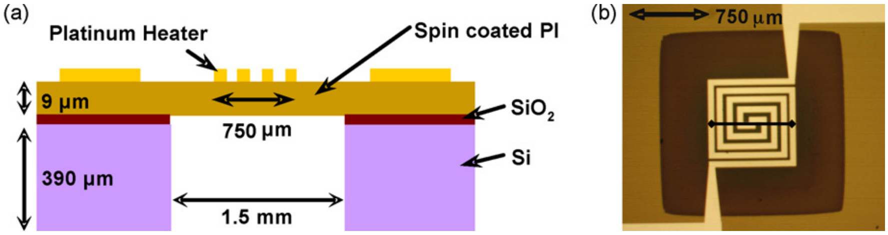

Fig. 6. (a) Cross-section view and (b) top view of a micro-hotplate on silicon with a polyimide membrane (1.5 mm wide, 9 µm-thick) and a Pt heater on top. The device was used to calibrate the thermal conductivity of the PI spun layer based on thermal simulations coupled with experimental temperature measurements.

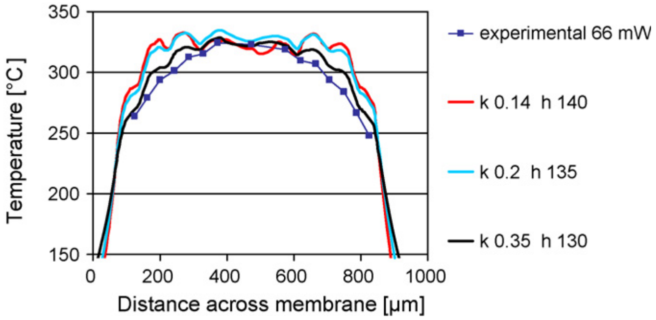

Fig. 7. Temperature distribution over the sensing area of the polyimide micro-hotplates described in Fig. 6b obtained by thermal simulations (using different values of the PI thermal conductivity in $\mathrm{W\,m^{-1}\,K^{-1}}$ and adjusting h in $\mathrm{W\,m^{-2}\,K^{-1}}$) compared to the experimentally measured temperature values at 66 mW.

shown by a simple peeling test we performed using scotch tape (3 M green). Moreover, after the annealing, the resistance value of the heater proven to remain relatively stable for several days at the operating temperature of 325 °C during the gas tests that were performed on these devices. The integrity of the hotplate was preserved during the annealing of the tin oxide coating. The sensors were also surprisingly mechanically stable, a relatively large bending of the plastic platform was necessary to have the tin oxide drop pumping off the substrate.

The electrical resistance of the Pt heaters of the PI hotplates made on silicon were respectively of 85 Ω. A slight variation of the resistance value within 1–2% occurred during the annealing of the gas sensitive coating, being more stable than the Pt/Cr metallisation, but with the drawback of a worse adhesion on PI.

3.2. *Thermal characterisation and simulations*

The temperature at the center of the active area as a function of the input power was measured using the micro-thermocouple described in Section 2. For sensors made on PI sheets, a temperature of 325 °C was reached at 130 mW. A better thermal insulation was provided by the thinner spin coated PI membrane on silicon, with a temperature of 325 °C reached at 82 mW. At these temperatures the thermal time constants were in between 250 and 400 ms depending on the design tested.

To determine the thermal conductivity of the spin coated PI, $k_{\mathrm{PI\,2731}}$, thermal simulations on the simple PI micro-hotplates made on silicon (Fig. 6) were performed and the results are presented in Fig. 7. The values of $k_{\mathrm{PI\,2731}}$ were varied, starting with the estimation provided by the manufacturer at a value of $0.14\,\mathrm{W\,m^{-1}\,K^{-1}}$, to match the temperature profile obtained from the experimental temperature measurements. The simulated profile matched better the experimental results when the value of $k_{\mathrm{PI\,2731}}$ was increased. To compensate the related decrease in temperature, the coefficient of convection was reduced to compensate the increase heat loss by conduction. This slight variation of the coefficient of convection had no influence on the simulated temperature profile obtained for a given $k_{\mathrm{PI\,2731}}$. Following these iterations, the thermal conductivity of the spin coated PI 2731 was defined to be of $0.35\,\mathrm{W\,m^{-1}\,K^{-1}}$ with a convection coefficient, h, of $130\,\mathrm{W\,m^{-2}\,K^{-1}}$.

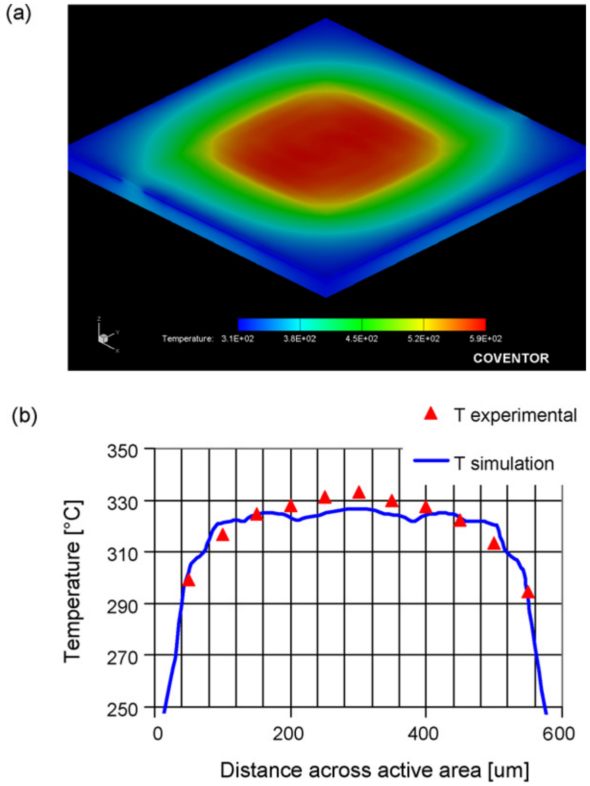

Fig. 8. (a) Simulated temperature distribution over the active area of a micro-hotplate made on a polyimide sheet (as shown in Fig. 1a) at an operating temperature of 325 °C. (b) Comparison of the simulated and experimentally measured temperature values over the active area of a micro-hotplate on a polyimide sheet. Simulations parameters: $k_{\mathrm{Upilex\ sheet}}$: $0.28\,\mathrm{W\,m^{-1}\,K^{-1}}$, $k_{\mathrm{PI\,2731}}$: $0.35\,\mathrm{W\,m^{-1}\,K^{-1}}$, h: $130\,\mathrm{W\,m^{-2}\,K^{-1}}$.

Double meander heating elements with an optimized homogeneous temperature distribution on Upilex sheets were designed using thermal simulations based on the thermal conductivity of the Upilex sheet provided by the manufacturer ($k_{\mathrm{Upilex\ sheet}}$: $0.28\,\mathrm{W\,m^{-1}\,K^{-1}}$) and on the one from the PI 2731 ($k_{\mathrm{PI\,2731}}$: $0.35\,\mathrm{W\,m^{-1}\,K^{-1}}$) evaluated in this study (see Fig. 8a). The thermal simulation was validated by using the micro-thermocouple and by performing a scan over the active area of the sensor. The comparison along the axis passing by the center of the active area, as presented in Fig. 6b, is shown in Fig. 8b. A good agreement is obtained between the simulated and the measured temperature values confirming the good estimation of the thermal conductivity of the spin coated PI film, at $0.35\,\mathrm{W\,m^{-1}\,K^{-1}}$.

3.3. *Gas measurements*

The sensors have been operated under the gas cycles described in the experimental section for few months. Even the sensors made on silicon with bent PI membranes demonstrated a good robustness. The performances of the sensors were comparable to silicon nitride hotplates coated with the same tin oxide paste. The measurements in Fig. 9 show the result of one typical sequence, proving that the sensors have been successfully produced with the described concept. In the gas measurements

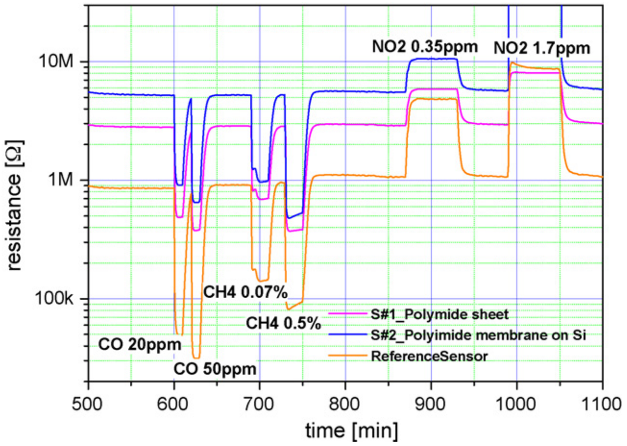

Fig. 9. Gas measurements under CO, NO_x, and CH_4 (50% Rh) using tin-oxide sensors on polyimide hotplates (PI sheet and silicon as substrate) and a reference sensor on a silicon nitride micro-hotplate.

presented, relatively slow recovery times can be seen, which are related to the gas mixing station and the chamber set-up. The small difference in the gas responses of the MOX sensors made on PI and of the MOX reference sensor made on silicon could be attributed to lower annealing temperature (450 °C) of the gas sensitive film for the sensors made on PI. Another contribution, probably less significant, could come also from a slight difference in the operating temperature of the devices due to the precision of few Celsius degrees of the calibration method used.

Gas tests have been performed on the devices packaged with the WLP concept with more or less success. The gas response for the MOX sensors packaged using the WLP concept exhibited a smaller response than the “opened” sensors on PI hotplates. It was noticed that the surrounding rim was too thin and therefore the gas permeable membrane to close to the MOX drop. The heat dissipated by the sensor caused the degradation of the membrane and a decrease of the baseline resistance of the sensor and in meantime of the gas response. The minimum distance required in between the drop and the gas permeable membrane for the proper operation of the sensor needs to be determined and the PI rim thickness adjusted accordingly. Nevertheless, the WLP principle has been proven before to work with standard MOX gas sensors fabricated on silicon [9,11]. Here the concept was extended to the sensors made on polymeric substrate, on which the WLP procedure is simplified by using the extra spun UV photopatternable PI layer as rim instead of having to micromachine and bond a Pyrex wafer, as described in references [8,9].

4. Conclusion

The integration of MOX gas sensors on PI micro-hotplates made on PI sheets and silicon as substrates was demonstrated. The hotplates made on PI sheets are simpler to process and more robust. Compared to the PI hotplates on silicon substrates, they are more suitable for the integration of gas sensitive MOX films. Tin oxide thick films were deposited using a drop coating method on PI platforms with patterned platinum heater and electrodes. The annealing of the drop in air was limited to 450 °C. The short-term gas sensing performances (few months) of the devices are encouraging. A wafer level packaging technique using multiple polymeric layers was developed to have a complete flexible platform. The technology is promising for the integration of PI humidity sensors, of resistive and capacitive gas-sensitive polymeric films to realise flexible gas sensor arrays.

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Biographies

D. Briand received his BEng degree and MASc degree in engineering physics from École Polytechnique in Montréal, in collaboration with the Laboratoire des Matériaux et du Génie Physique (INPG) in Grenoble, France in 1995 and 1997, respectively. He obtained his PhD degree in the field of micro-chemical systems from the Institute of Microtechnology, University of Neuchâtel, Switzerland in 2001, where he is currently a team leader. He is in charge of European and industrial projects, of the supervision of doctoral students and has teaching assignments. His research interests are in the field of Microsystems include the development of polymeric and power MEMS and the integration, packaging and reliability of micro-chemical sensors.

J. Courbat received his MSc degree in microtechnology from the Swiss Federal Institute of Technology, Lausanne (EPFL) in 2005. He currently works as a PhD student in the Institute of Microtechnology, University of Neuchâtel, Switzerland. His research activities are focused on the integration of gas sensors on flexible substrates.

S. Raible received the PhD degree from the Eberhard Karls University of Tuebingen, Tuebingen, Germany, in 1999, in the field of scanning probe microscopy. From 1999 to 2000, he was with the Institute of Physical Chemistry, Eberhard Karls University of Tuebingen, working on new coating technologies for micromachined gas sensors. In 2000, he cofounded Advanced Sensing Devices, which merged with AppliedSensor GmbH in 2001. Since then, he has been working on the development of micromachined metal oxide gas sensors and is responsible for the mass production buildup. His research activities are in the field of microsystems, especially in the field of gas-sensing applications.

J. Kappler received the MASc and PhD degrees in physics from the Eberhard Karls University of Tuebingen, Tuebingen, Germany, in 1997 and 2001, respectively. From 1996 to 2001, he was with the Eberhard-Karls University of Tuebingen, working in the field of semiconductor gas sensors. In 2001, he cofounded Advanced Sensing GmbH, which he headed as Chief Executive Officer until its merger with the Applied-Sensor group in 2004. Since then, he has been heading all sensing component activities within the AppliedSensor group. AppliedSensor sensor technologies comprise micromachined semiconductor gas sensors, field-effect sensors, and quartzmicrobalance sensors.

N.F. de Rooij received PhD degree from Twente University of Technology, The Netherlands, in 1978. From 1978 to 1982, he worked at the Research and Development Department of Cordis Europa N.V., The Netherlands. In 1982, he joined the Institute of Microtechnology of the University of Neuchâtel, Switzerland (UniNE-IMT), as professor and head of the Sensors, Actuators and Microsystems Laboratory. Since October 1990 till October 1996 and from 2000 up to now, he has been acting as director of the UniNE-IMT. Since 1987, he has been a lecturer at the Swiss Federal Institute of Technology, Zurich (ETHZ), and since 1989, he has also been a professor at the Swiss Federal Institute of Technology, Lausanne (EPFL). His research activities include microfabricated sensors, actuators and microsystems.