Introduction

The aim of this international project is to develop a smart hybrid gas multi-sensor module for environmental applications, i.e. by combining thick-film, thin-film and polymer-film sensor elements with a signal processing ASIC within a single package, which should be useful for all sensor types. The module should enable multi-sensor operation as well, when connected to an intelligent signal-processing unit. The sensor module has a number of advantages including the possibility of minimizing temperature, humidity and gas compound interference effects. The ASIC converts the sensor resistance into an industrial standard current signal (4-20mA), which makes the smart sensor module easier to use in industrial environments. The main components of the module also determine the design directions as follows:

• the ASIC chip;
• the sensor resistor elements; and
• the package.

1. System concept

The block diagram of the intelligent gas sensing measurement set-up is illustrated in Figure 1. The ASIC involved here has the aim of converting the resistivity changes (most likely within the range of $10^2-10^5$Ω) of the gas sensor elements into an electrical signal. This is a 4-20mA current loop signal, which avoids the influence of connecting cable resistance values. The sensor resistor element is compared with a reference resistor to compensate for some undesired environment effects, such as temperature fluctuations. The ASIC contains a preamplifier, a low pass filter and a voltage-to-current (V-I) converter. To provide the widest flexibility, and uniform packaging and electrical connections for sensor elements of different nature, the following system assembly considerations were met:

• sensor modules will be packed individually in the first approach;

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a single module contains the following elements: one gas sensor with one reference resistor, one signal conditioner ASIC, and an optional heating supply circuit where necessary;

- an array of such modules will be built up by fixing them on a motherboard and connecting them to the data transmission, multiplexing and data acquisition units;

- intelligent functions are added from outside of the modules;

- the ASIC may also contain some multiplexing capability for future extension purposes, enabling the integration of sensor arrays inside the same module.

2. ASIC design

A 2μm-resolution HBIMOS technology has been selected for the design of the ASIC (available at Alcatel Mietec). This technology is aimed at the automotive market and therefore offers a combination of MOSFET, bipolar and DMOS devices with voltage ranges from 5 to 100V. The MOSFETS can operate up to 15V and are particularly useful for our purposes as they combine small size and sufficient voltage range.

The circuit proposed here is a folded version of the classic bridge, followed by a V-I converter. One of the advantages is that the voltage signal is proportional to the ratio of the reference resistor and the sensing resistor. The core of the ASIC is the design of a MOS operational amplifier. The amplifiers used only have to cope with low frequency signals, so that bandwidth is of less concern. The operational amplifier circuit layout is based on a design described in Eynde et al. [1]. The circuit topology chosen allows high linearity and high output current. The operational amplifier features an AB output stage to guarantee linearity and to drive the relatively important resistive loads. The operational amplifier has a pull-down feature, allowing different amplifiers to be driven from the same output pad; the pull-down feature forces the output to become high impedance by pulling the gates of the output transistors to their respective source voltages. This can be used for reducing power consumption, but also for multiplexing the outputs of several operational amplifiers, allowing arrays of sensors to be connected to a single ASIC (single signal output). At the layout level, several blocks are common to the different signal conditioners; e.g. the bias circuit and reference sources are common to all amplifiers. Furthermore, as only one of the output V-I converters should be operating at the same time, silicon area can be saved by multiplexing the outputs of the intermediate “voltage adjusting” amplifiers to a single V-I converter block. The amplifier supply voltages are −6V and +6V, with an output voltage range between −5V and +5V. The common mode input range must fit these data as operational amplifiers are used in cascade: both a p and n differential input pair are used to accommodate this requirement.

Simulations show an operational temperature range of 0 to 80°C. The ASIC must feature temperature invariability as the heated gas sensors and ASIC are intended to be assembled into a single package.

3. Gas sensor resistor research

Gas sensor resistor array research and development is being undertaken in three directions at three different research centres in order to get a wide variety of behaviour and also a number of possible gas compounds to be monitored. The main sensor element types should be based on the following technologies and materials:

- thin-film SnO₂ resistor elements operated at high temperatures;
- thick-film SnO₂ resistor elements prepared from organo-metallic pastes and operated at high temperatures;
- electroactive conducting polymers (ECPs) deposited electrochemically or chemically on thick-film substrates operated at room temperatures.

A common property of all three types is that the sensor elements are resistors. They can be used to sense gases and vapours by monitoring...
the changes in conductance on exposure of the films to the gas sample.

### 3.1 Thin polycrystalline SnO₂ film gas sensors

Over the past few decades, solid-state gas sensors based on SnO₂ have become the predominant solid-state devices for gas alarms used in domestic, commercial and industrial premises [2,3]. Even sensor arrays have been fabricated using exclusively inorganic materials of the same nature [4]. The detailed analysis of the extensive literature is out of scope here, although we give some new references [2-6].

The original construction of the thin film gas sensors proposed in this work is shown in Figure 2. It consists of two resistors with interdigital finger structures, having three contacts: one contact of the two resistors is common. The heater meander surrounds both elements to provide equal temperature for them. A thin SnO₂ film is deposited onto the surface of the substrate over the interdigital electrodes and ought not to cover the heater. Such a structure permits the device to work as a differential sensor when a protective dielectric film (SiO₂, Al₂O₃, and MgF) covers one of the two resistors for reference purposes, or it is doped with some impurities for varying the selectivity.

The contacts and the heater were fabricated from a vacuum evaporated Cr bottom adhesion promoter layer and a sputtered Pt on the surface of 25 × 25-mm-area mica or quartz substrates. The thickness of the mica substrate was about 80-120µm and that of the quartz was 200µm. The sensor structure has a size of 12.5 × 12.5mm. So one substrate includes four sensor elements. The sensor pattern was formed by photolithography.

SnO₂ thin films were prepared by reactive sputtering from a pure tin target (99.99 per cent) in an atmosphere of 88 per cent Ar / 12 per cent O₂. The deposition of the films was conducted through a stainless steel mask. The temperature of the substrates during the deposition of SnO₂ films was 400°C.

### 3.2 Thick-film organo-metallic resistor elements

SnO₂ based sensors can also be fabricated by standard thick-film technology using organo-metallic pastes that provide the raw material of the resistor through chemical decomposition-oxidation processes during firing. Since the sensor elements have working temperatures at about 450°C, a careful selection of materials is necessary in order to produce a system with long-term reliable operation without drifts due to ageing. The design of the sensor could be split into two main tasks: the first problem represents the design of the sensorial part and the second poses the sensor heater resistor.

The principle of gas sensing is based on reversible molecular interactions on the active surface of SnO₂. This is why the specific surface, i.e. the ratio of effective surface and film volume could be minimised. Thick-film technology for sensor production can not fully respect this demand. This fact could cause increased interference reactions in comparison with thin film sensors.

The model of gas sensing mechanism in grainy semiconductor thick-film SnO₂ layers is well described in the technical literature [7,8]. The adsorbed oxygen molecules remove conduction electrons from the grain boundaries, thin depletion layers are created on the surface of the grains. The energy barrier between the grains is modulated if a combustible gas compound removes oxygen ions from the surfaces. The result will be a measurable resistance variation.

Chemical compounds, like Pt or Pd may catalyse the gas sensing by two major mechanisms: concentrating reaction constituents onto the active surface and decreasing the level of activation energy by influencing the Fermi energy level inside the semiconductor [6]. It is obvious that the exact preparation of raw materials for the sensor layer has a determining influence on the sensor’s behaviour. Sensor arrays have already been fabricated mainly by two approaches: varying additives or operating temperature of sintered thick-film tin-dioxide resistor elements [9].

Design of the sensorial part is based on the idea that both surfaces of a sensor substrate will be used: top side for the sensing part, and back
side for the heating element. The idea to collocate both parts on the one side of the substrate is unsuitable for manufacture using standard thick film technology. The layout of the sensorial part is shown in Figure 3(a). The resistance of the SnO₂ layer is measured between interdigital Au electrodes. Two elements are realised: one for the sensor and the other for the reference resistor. The latter one is covered by a film to prevent reactions with gas compounds.

Generally, the heater has an important effect on gas sensors because the working temperature is relatively high, and its distribution on the substrate surface must provide equal temperature for the overall sensor and reference resistor film. The heating element is placed onto the backside of the sensor substrate. Thermal modelling was used to optimise its structure which is illustrated by Figure 3(b). One simple solution is to apply a number of thick film thermistor resistors connected in parallel. The eventual result of this design is drawn in the Figure: it represents one conductive layer with interdigital structure and a simple resistive layer, which generates the demanded system of parallel resistors in this layout.

3.3 Conducting polymer film based sensors

At the beginning of the 1980s, the ultimate property of most polymers, which distinguishes them from metals, was their inability to carry electricity. Electrical conductivity was introduced into these materials by adding conductive grains to form a metal/polymer composite, or by the incorporation of ionic species to form polymer electrolytes. During the past 20 years, a new group of organic polymers has been revealed with the ability to conduct electrical current inherently. These electroactive-conducting plastics (ECPs) are still under development for appropriate applications, such as rechargeable batteries, capacitors, field-effect transistors, enzymatic biosensors, and gas sensors. They may offer a number of advantages over conventional inorganic based sensors. Because of their very unique and specific behaviour, they are considered intelligent material systems. The aim of the research in the frame of this international project is to find a practical exploitation of the special properties of these type of materials by completing the system of inorganic gas sensor resistor materials with ECPs and thus introducing new potential possibilities into the targeted intelligent gas monitoring system.

ECPs can easily be synthesised and deposited onto conducting surfaces by a simple electrochemical polymerisation method, where the doping reaction modulates the conductivity reversibly via redox interactions. Electroconducting conjugated polymers are good candidates for the elaboration of chemical or electrochemical sensors in two ways: either as a matrix for immobilisation of active compounds or as sensitive components, where some properties of the polymer film changes in presence of the studied phenomena. The electronic conductivity related to the doping level of an ECP is modulated by the interaction with various substrates and analytes. The incorporated doping ions or other species transmit film and environmental interactions.

A variety of devices have been developed and constructed utilising the reversibility in redox properties of ECP films, coupled with the incorporation of electrolyte anions into the polymer film, and dissolution of them which may take place in the redox reaction. Therefore, conducting polymers can also be used to sense gases and vapours by monitoring the change in conductance on exposure of the polymer to the sample gas. Preliminary studies on these materials have shown that they exhibit a fast and reversible response even at room temperatures, which can not be

Figure 3 Layout build-up of the thick-film gas sensor: (a) topside with the sensor and reference resistors (A-conductor, B-sensor layer, C-protective layer); (b) backside with the heater (A-conductor, B-heating resistor film)
expected with inorganic films [10,11]. These polymers have a number of distinct advantages in the point of view of gas sensing:

- a wide variety of polymer materials is available;
- they can be formed by electrochemical polymerisation of the monomer under coulombmetrically controlled conditions;
- a number of doping materials can be incorporated;
- the thickness of the film is variable by changing the polymerisation time;
- the gas sensors should operate at room or close room temperatures;
- they are cheap enough to provide disposable sensor elements.

One disadvantage of these materials is their lack of specificity: they show responses to a wide range of different gases and vapours. Lots of ECPs were studied for use in gas sensors. They produce non-selective response to different gases [12-14]. On the other hand, their selectivity behaviour seems still to be better than that of the inorganic material based gas sensitive resistors. For example, polypyrrole showed a much higher sensitivity to methanol than to ethanol, and it is also highly sensitive to nitrous gas compounds, such as NH$_3$ and NO$_2$. These effects differ considerably from those found with inorganic SnO$_2$ based gas sensor resistors and give a good chance of improving the selectivity when combining organic and inorganic based sensor elements within an intelligent monitoring unit.

The conductor film should be realised first by conventional thick-film processing, applying screen printing onto 96 per cent alumina substrates. Since a resistor film should be created, two conductors with an isolation gap are necessary for this element. Since the resistor film is electrochemically deposited, its grow-through between the electrodes should be reached to form a real resistor film. Thus, a narrow gap should be fabricated between the electrodes the resolution of which can not be realised by conventional screen printing technology.

Therefore, a continuous film should be screen-printed first, and it should be divided by a gap made by laser engraving into the film. Thus, laser processing is necessary in the second main step of technology. The last step is the electrochemical deposition and grow-through of the polypyrrole to form a gas sensitive resistor film.

The layout in Figure 4 had to be completed with a special interconnection system that enabled the application of equal-potential surfaces on all the electrodes of one substrate during the electrochemical deposition. These auxiliary conductors and pads were removed from the sample by detaching the parts that are unnecessary for gas sensor operation. The output pad system corresponds to the standard pin arrangement. The overall size of the rectangular-shape element is 5mm × 12mm which allows it to fit well together with a reference resistor into the window of the package shown in the following section.

3.4 Testing gas sensitive resistors

Gas sensitivity behaviour of thin- and thick-film SnO$_2$ resistors have been studied for many years and are well known from the literature [2-9]. In general, the prepared samples also followed this behaviour:

- Sputtered thin-film SnO$_2$ resistors showed very good sensitivity for CO and H$_2$, less sensitivity for hydrocarbons and alcohol vapours (operating temperature 350°C).
- Thick-film SnO$_2$ resistors are rather sensitive for hydrocarbons (especially for methane) and alcohol vapours, H$_2$, and less sensitive for CO. Their behaviour is rather uncertain for ammonia and NO$_x$ (operating temperature 450°C).
- $R_{gas}/R_0$ characteristics are close negative linear curves in a log-log plot.
- Sensor characteristics can slightly (but not significantly) be modified with precious metal additives into the material, or by varying the operating temperature between 350 and 450°C.
- A conclusion was drawn to use twin element sensor arrays when combining different behaviours for multi-component sensing.
Less information is available about gas sensitive ECP films\[10-14]. During our experiments, we concluded the following:

- Electrochemically and chemically deposited polypyrrole (PPy) films show good sensitivity for ammonia, less for methanol, almost no sensitivity for ethanol, and practically no sensitivity for other compounds mentioned above (operating temperature 25°C). Their characteristics are given in Figure 5.
- Electrochemically deposited polyaniline (PANi) films show extremely good sensitivity for ammonia, less for NOx and practically no sensitivity for other compounds (operating temperature 25°C).
- A conclusion was drawn to use twin element sensor (PPy and PANi) arrays when combining different behaviour for the multi-component sensing.

Thus, a combination of inorganic thin- and thick-film SnO2 with ECP film resistors should be a good candidate of gas sensitive resistor arrays for environmental multi-component sensing.

4. Packaging concept

Integrating sensor elements and the ASIC into the same module provides a great challenge for packaging. A number of requirements must be met, the package must assure:

- the minimal possible size for the overall module;
- a cost effective interconnection between the sensor elements and the IC;
- the protection of the ASIC chip from all environmental effects (gases, sensor heating, etc.);
- the minimal heat conductance between heated sensor elements and their environment;
- the possible inclusion of non-heated sensor elements;
- “gas transparency” for the monitored medium towards the sensor;
- “gas isolation” of the reference elements.

The designed substrate for the sensor module is shown in Figure 6.

The heated sensor elements are connected by wires to the module substrate. Polymer based sensors can directly be bonded onto the substrate. The sensor substrate may have a maximum area of 12 x 14mm. The contacts are gold plated to allow wire bonding. Eleven contacts are present on the substrates, five correspond to the sensor element connections. The sensorial part is closed with gas transparent stainless steel screens for mechanical protection. The ASIC is wire bonded and closed with globe-top packaging. Some surface mounted (SM) components are also soldered around it. The process flow is as follows: board manufacturing; solder paste printing; pick and place of SMDs; reflow soldering; cleaning; die bond adhesive dispensing; die bonding of ASIC(s); curing; wire bonding; first tests; globe top dispensing; curing; bonding of the sensor; prefabricated cap mounting; testing.

5. Conclusions

The main goal of this research is to find a new approach for multi-component gas sensing by combining a new type of organic conducting polymer based and conventional inorganic thin- and thick film metal-oxide sensor resistor elements. The first testing of the sensor resistor elements indicated that there might be a great difference in sensor responses which therefore allows for the fabrication of an array of sensors for highly effective multi-component sensing. The very different nature and operating conditions of the sensor elements needed a special concept for the array design: sensor elements are individually combined with an ASIC signal conditioner for getting compatible output signals. Packaging
design must also be flexible enough to allow for uniform outlines with different sensors. All these issues have been discussed in the paper. A real multi-component sensing test now requires that we connect the smart elements into an intelligent signal processing system and this is the subject of our ongoing research.

References