RESPONSE TIME OF HYDROGEN SENSORS

Hübert, T. and Banach, U.

BAM Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin, Germany, Thomas.huebert@bam.de

ABSTRACT

The efficiency of gas sensor application for facilitating the safe use of hydrogen depends to a considerable extent on the response time of the sensor to change in hydrogen concentration. The response and recovery times have been measured for five different hydrogen sensors, three commercially available and two promising prototypes which operate at room temperature. Experiments according to ISO 26142 show that most of the sensors surpass much for a concentration change from clean to hydrogen containing air the demands of the standard for the response times $t_{(90)}$ and values of 2 to 16 s were estimated. For an opposite shift to clean air, the recovery times $t_{(10)}$ are from 7 to 70 s. Results of transient behaviour can be fitted with an exponential approach. It can be demonstrated that results on transient behaviour depend not only from investigation method, and the experimental conditions, like gas changing rate and concentration jump, as well as from operating parameters of sensors. In comparison to commercial MOS and MIS-FET hydrogen sensors new sensor prototypes operating at room temperature possesses in particular longer recovery times.

1.0 INTRODUCTION

Fast response to a change of gas composition is one of the key properties for assessing the suitability of sensors for hydrogen safety. Response and recovery time are commonly used terms to define the speed of response of gas sensors. According to ISO 26142 the time of response is defined as the interval, with the sensor in a warmed-up condition, between the time when an instantaneous variation between clean air and the (hydrogen containing) test gas, or vice versa, is produced at the sensor inlet, and the time when the response reaches a stated percentage of the stabilised signal on the standard test gas [1]. The time taken for a sensor to reach 90 % of the final indication (response time or t_{90}), when exposed to a certain hydrogen concentration, shall be less than 30 s. Conversely the time taken for a sensor to reach 10 % of the preceding response (recovery time or t_{10}), following exposure to air shall be below 60 s [1]. These values for hydrogen sensor response and recovery time may be considered by some as too long for application and in fact several hydrogen sensors have response and recovery times of only a few seconds.

Precise measurement of short times of response and recovery is not easy to do and requires some experimental efforts. Recording of a sensor's dynamic behaviour, can be misleading, e.g. because the determined signal change is not caused by the intrinsic reaction mechanism of the sensor, but by a retarded change of test gas concentration. The influence of different methods of determination and specific arrangements are discussed in detail by Brett et al. [2]. From an experimental point of view, the results of investigation of dynamic behaviour of sensors can be separated in two parts, an intrinsic and an extrinsic time of response. The extrinsic time reflects the dynamic behaviour of test gas supply to the sensor inlet and of the data acquisition system for sensor signals and can results in a certain delay time. The intrinsic response time is determined by the physico-chemical sensor element as a transducer of chemical composition into an electrical signal and by the primary measurement circuit. Thus for experimental investigations it is necessary to determine the transient behaviour of the gas supply, whereas the electronic data collection which are supposed to be not more than some µs, can be mostly neglected.

A transfer function of the sensor element can be derived and the transient gas sensor signal can be modelled by a sum of exponential functions [3]:

$$S(t) = \sum_{i=1}^{n} G_i \cdot \exp(-t/\tau_i) \qquad (1)$$

For practical reasons, the number of exponential functions will be restricted. Only one function is sufficient to describe the time of response of semi conductive metal oxide (MOS) sensors, whereas for fast responding field effect sensors two exponential functions give a better approximation [4, 5]. Assuming that after a transient period, the sensor at a constant gas composition always delivers a time constant signal *S*, then due to an instant change of gas concentration the increasing or decreasing time dependent sensor response *S*(*t*) can be described as follows [6]:

$$S(t) = \begin{cases} S_0 & t \le t_s \\ S_0 + (S_1 - S_0)(1 - \exp(-t/\tau)) & t > t_s \\ S_0 + (S_1' - S_0')(\exp(-t/\tau') & t > t_s' \end{cases} \qquad (2)$$

S_0 and S_1 are the final sensor signals before and after a change of gas concentration resulting in an increase of the sensor signal. S'_1 and S'_0 are the signals before and after a change of gas concentration with decreasing value of sensor signal. t_s and t'_s are the times when a change of sensor signal starts and τ and τ' are the respective time constants. Both functions can be used to estimate the response and the recovery time, however is has to be considered that t_s and t'_s can include an intrinsic time delay of sensor response. In case that according to the definition of time of response given above, pure air is used, S_0 and S'_0 can be adjusted to zero and the equation is similar to transfer function of a low-pass filter.

The aim of the paper is to evaluate experimental measurements of hydrogen sensor response and recovery times in one facility under comparable conditions. We discuss the extrinsic contributions of the facility on transient response, as well as the intrinsic sensor related contributions to sensor signal response. For this investigation five different sensors are chosen, three are commercially available and are two promising sensors under development. The development of these sensor prototypes is aiming to reduce their energy consumption while lowering working temperature and detection limit. However the ambivalent impact of sensor development in relation to response and recovery time is not so evident.

2.0 EXPERIMENTAL

2.1 Sensors

Two commercial semiconductor MOS-type sensors of different performance were tested (MOS I), (MOS II). Its sensing principle is based on the change of the conductance of a heated doped metal oxide semiconductor (SnO_2) thick film on a ceramic substrate due to the absorption of hydrogen. Also a sensor based on a metal-insulator-semiconductor field effect transistor was investigated, where the change of work function as a result of hydrogen absorption on a palladium thin film is exploited (MIS-FET). The investigation includes two prototypes of new upcoming sensors; a Schottky diode (RT-Diode) and a field effect based sensor (RT-FES). Both prototypes operate at room temperatures and have low power consumption which may give advantages in various applications.

2.2 Sensor Testing Facility

The measurements were made using the BAM test gas system GASI (see Fig. 1a). The facility consists of a computer controlled mixed test gas generation tool with a climate chamber for adjusting the gas temperature in the range of -40 to 180 °C and a data acquisition system using a network analyser HP 4194A. A schematic overview is given in Fig. 1b.

The test system provides independent mixing of gases together with humidification in a dynamic range of 10 to 1000 sccm/min. Gas mixing is performed via mass-flow controllers (MFC). The system is able to prepare gas mixtures containing up to four test gases, an inert carrier gas (synthetic air or nitrogen) and humidity. The humidification of the gas mixture in the range of relative humidity from 0.05 % to 99 % is based on the saturation method with a glass bubbler. The humidified carrier gas is cooled down in a gas cooler to adjust the dew point. Finally, the humidified carrier gas is mixed with

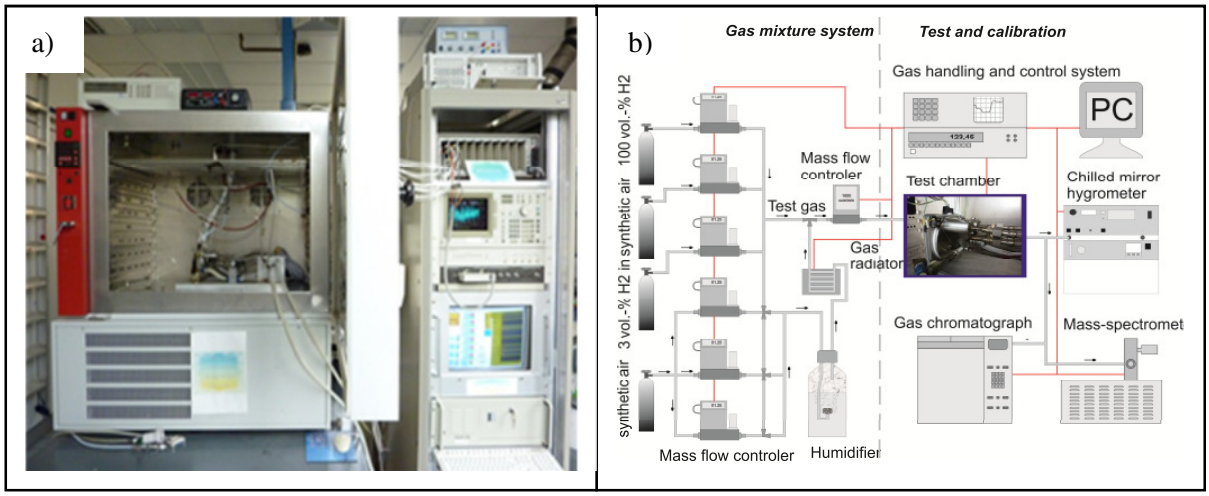

Figure 1. BAM testing facility (a - photograph, b - schema)

the test gas; dry inert carrier gas is added. Thus pure hydrogen or hydrogen containinggas mixture in air is diluted in air and in most experiments the flow is adjusted to 1000 sccm/min. The exhaust gases can be analysed by dew-point mirror hygrometer, quadruple mass-spectrometer and gas chromatograph to check gas mixing and the actual gas concentration. The stainless steel supply lines have an inner diameter of 6 mm and Swagelok connections. A personal computer controls all parts of the system via an IEEE-bus net using a programme based on LabView both for gas generation and gas concentration time test program as well as for data acquisition.

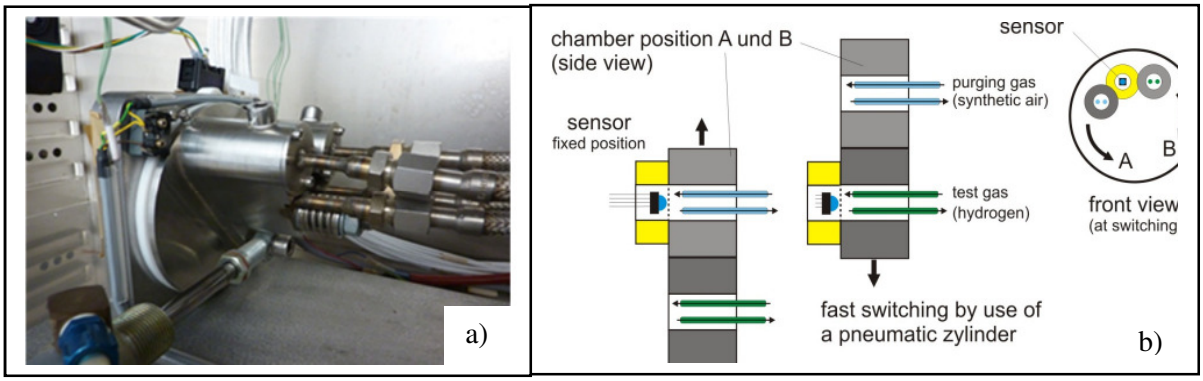

Figure 2. Dynamic test chamber for sensor testing (a – photograph, b – schema)

Sensors were placed in a stainless steel test chamber and blown by a laminar flow (method 1). The calculated delay time of this method, which includes the time needed for switching of the gas valves and the time required to provide gas flow at the desired concentration at the sensor inlet, is 4 s. For testing sensors of very fast time of responses, a dynamic test chamber with pneumatic switching was used. The circular designed and optimized tool which has a volume of 5 cm^3 is shown in Fig. 2a (method 2). The material of the test chamber is stainless steel (electro polished), combined with insulating PTFE for the sensor sockets. In order to realise a quick exchange of gases on the sensor inlet, the device provides two simultaneous streams of gas flowing alternatively to the sensor. By pneumatic switching from a gas A to a gas B rotate the sensor from one test gas concentration to another (see Fig. 2b). The delay time is at least 200 ms assuming conditions of a plug flow reactor. The sensors were tested at room temperature of (23° ± 1) °C.

The data acquisition which requires precise measuring tools (digital multi meter or network analyser) for sensor signals, like voltage, current or resistance was adapted to the specific hydrogen senor-type. The measuring interval was 0.7 or 1 s with a resolution of 100 ms. The use of a CAN-bus allows time

intervals for data acquisition of 100 ms and a resolution of 10 ns. The data were evaluated and plotted with Excel and Origin programs and response time $t_{(90)}$ and recovery time $t_{(10)}$ were calculated from the sensor response and recovery curves.

3.0. RESULTS

Typical response and recovery curves of a hydrogen sensor are shown in Figure 3. Even though a very fast first response can be observed, a delayed sensor signal increase or decrease is detectable. Then the signal changes rapidly; however it can demand a remarkable long time span to reach the final indication.

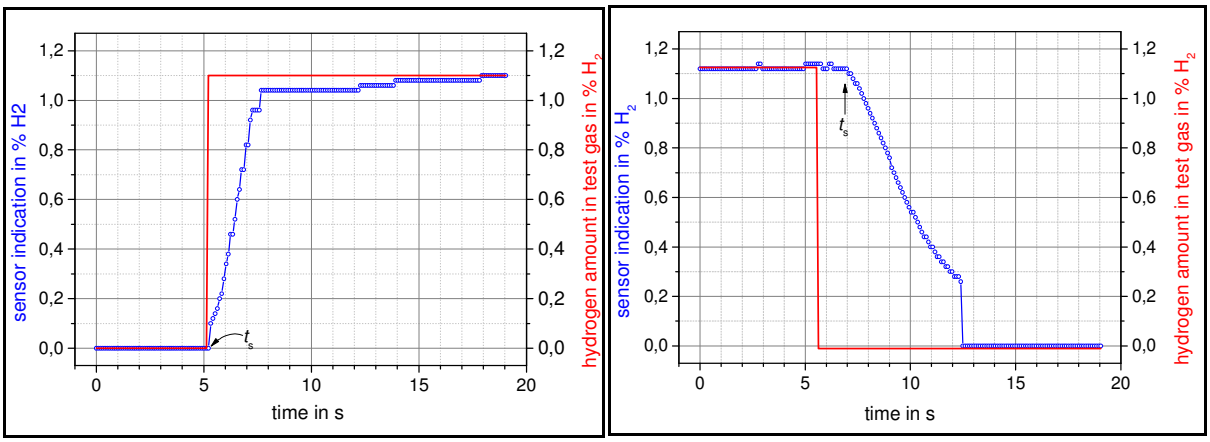

Figure 3. Fast response (a) and recovery (b) curves of time of the MIS-FET sensor as obtained by method 2 (switching the dynamic test chamber) with data output from CAN-bus (reading every 100 ms, resolution of 10 ns)

As a result of investigations of dynamic behaviour of the five sensors, response and recovery times were calculated taking into account the respective (extrinsic) time delay of the facility. The data were collected in table 1. Always a time interval is given because a data scattering occurs even by repeating the measurements under identical conditions and especially by variation of the concentration jump. Aging of sensor can induce an increase in sensor response and recovery times.

Table 1. Response and recovery time of tested hydrogen sensors.

Sensor	**Response times $t_{(90)}$ (s)**	**Recovery time $t_{(10)}$ (s)**	**Method**
MOS I	2 - 6	10 - 12	2
MOS II	5 - 16	13 - 50	2
MIS-FET	3.3 - 3.5	10.2 - 10.3	1
	2.1 - 2.3	6.8 - 6.9	2
RT Diode	150 - 200	100 - 300	1
RT FES	10 - 15	50 - 70	1

4.0 DISCUSSION

4.1 Contributions to delay time of sensors

A retardation of sensor signal generation is caused by several effects, here divided in three parts and illustrated in Fig. 4. First, the extrinsic time due to the electronic time constant for valves switching and time of gas flow to fill the gas pipes and the test chamber till the sensor inlet is reached. For method 1 this requires around 4 s at a gas flow rate of 1000 sccm/min. It includes also the assumption of a laminar flow and that this new gas concentration immediately reaches the sensor inlet. The extrinsic time delay for the pneumatic switching test chamber, which has a smaller volume, is only around 200 ms. The intrinsic time response of the sensor consisting of certain dead time and a continuous signal shift to final indication results from the time constant of the physico-chemical reaction on or in the sensor element and the time constant for the change of the electrical signal. This can be discussed by a diffusion based model [7]. The time constant of the primary measuring circuit of the sensor for signal transformation, amplification is assumed to be below 10 ms and can be neglected. Also the time constant of the electronic units for measurement of the sensor output and display is expected to be < 10 ms and will not be considered in the following.

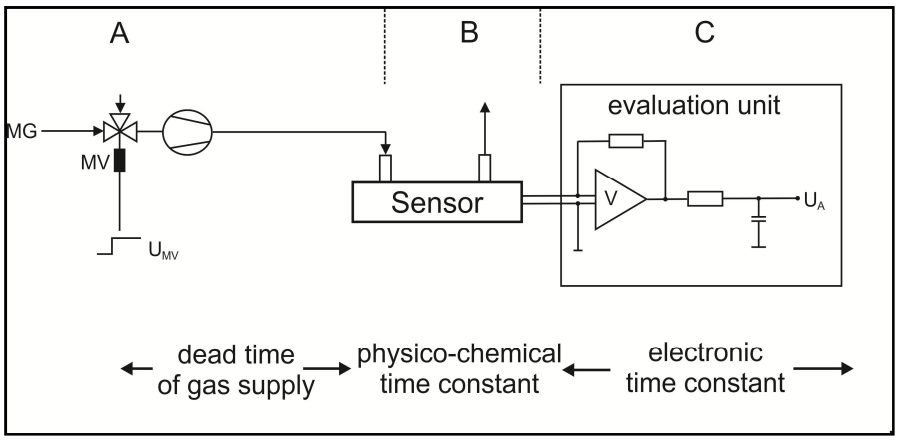

Figure 4. Three parts of for time delay in sensor testing

4.2 Comparison with results from literature

The compilation in table 2 shows that the obtained results on response and recovery time (see table 1) are comparable with data from literature, even though some data are little blurred. Also the quickest measurements of response time, performed with switching the pneumatic test chamber of 2.1 s to 2.3 s and 6.8 s to 6.9 s of recovery time are comparably with those times claimed by the sensor manufacturer of < 2 s and < 10 s (see table 2). The values for the response times given in [2] are in very good coincidence.

Table 2. Response and recovery time of commercial hydrogen sensors.

Sensor type	Response	this work (s)	results from literature (s)	source
MOS	$t_{(90)}$	2 - 6	16 ≤ 15	[8] [9]
	$t_{(10)}$	10 - 12	12 < 30	[8] [9]
MIS-FET	$t_{(90)}$	2.1 - 2.3	< 2 2 - 4	[10] [2]
	$t_{(10)}$	6.8 to 6.9	< 10 9.2	[10] [2]

4.3 Influence of hydrogen concentration on step response

Influence of gas concentration on measured response and recovery times is reported in literature [2, 4, 11]. Measurements of new MOS sensors, made as part of this work, demonstrate a faster transient behaviour and may reflect progress in senor technology development. As shown in Fig. 5, a non-linear behaviour can be observed what can be approximated with a logarithmic approach. In many cases MOS sensors show, after a concentration step, a small long time signal drift till a final constant indication is reached. This effect has a stronger influence in respect to the total signal change for lower concentration changes, which may explain the decrease of response time measured in higher hydrogen concentrations.

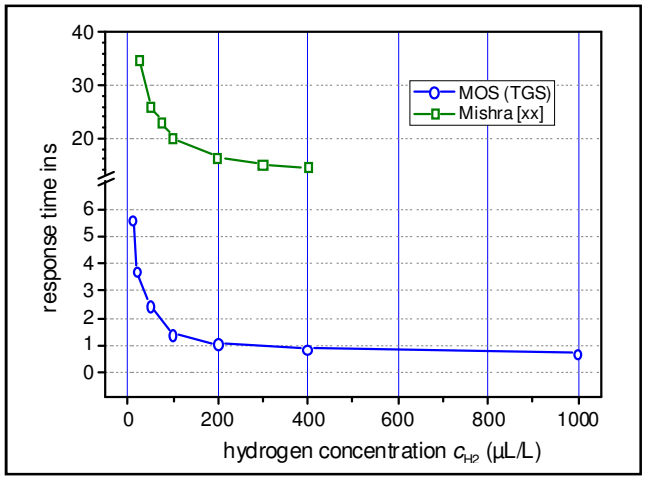

Figure 5. Response time versus hydrogen concentration for MOS-type sensors

4.4 Modelling of response and recovery time

In order to compare the results from sensors which are delivering different signals, the following transformation according to equation 2 was performed:

$$S_r(t) = \frac{(S(t)-S_0)}{(S_1-S_o)} \qquad (3)$$

The normalised sensor signal for increasing and decreasing hydrogen concentration displayed in Fig.6.

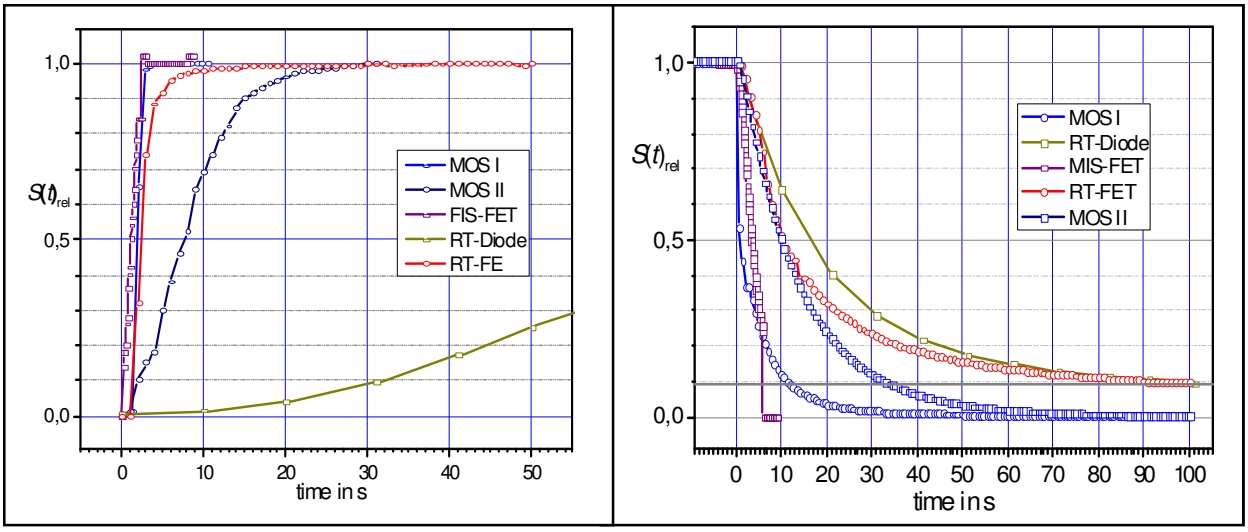

Figure 6. Time response (without sensor delay time) of hydrogen sensors for increasing and decreasing concentration

Measured data were fitted according to equation (2) and results are collected in table 3. The Parameters τ and τ' are the constants and characterizes the sensors signal change for increasing and decreasing hydrogen concentration. The delay time was not considered. Therefore the values for response and recovery time in table 1 are a little longer. A sufficient correlation coefficient was obtained, what may support the plain assumptions about the transfer function; however a better fit was obtained for the recovery time by using a model with two exponential functions, as already described for FET based sensors [5]. The improved approximation does not necessarily have a physical meaning and can be due to the larger number of parameters.

Table 3. Results of data fitting.

Sensor	Response time $1-\exp(-t/\tau)$		Recovery time $\exp(-t/\tau')$	
	τ	r	τ‘	r
MOS I	2.1±0.1	0.90	4.1±0.2	0.94
MOS II	14.7±0.1	0.99	75±4	0.96
MIS-FET	1.5±0.1	0.98	6.3±0.6	0.91
RT Diode	81±3	0.99	45±4	0.92
RT-FES	2.9±0.2	0.96	22.3±1.4	0.94

5.0 SUMMARY

The tested commercial and prototype hydrogen sensors possess, with one exception, remarkable fast times of responses and recovery and fulfill the demands of ISO 26142 in this area. The investigation demonstrated the influence of the testing facility and method and experimental parameters on hydrogen sensor response and recovery time measurements. Defined experimental conditions are needed in order to obtain precise, reliable and comparable data. The shortest times of response were obtained with a pneumatically switchable test chamber. It was shown that the hydrogen concentration in which measurements were made also influences the results. The estimated values for response and recovery time indicate a different dynamic behavior of the hydrogen sensor related to their construction and sensing principle. Shortest response was yielded from field effect transistor, what may be plausible due to the decisive surface effect of hydrogen absorption on a thin film. Room temperature operation of hydrogen sensors has certainly advantages in respect to low power consumption, however the prolonged time recovery still have to be overcome. A fitting of time response data with a single exponential approach, comparable with a first order lag element, gives good accordance.

References

1. ISO26142:2010, Hydrogen detection apparatus.
2. Boon-Brett, L., Black, G., Moretto, P., Bousek, J., A comparison of test methods for the measurement of hydrogen sensor response and recovery times, *International Journal of hydrogen energy,* **35**, 2010, pp. 7652-7663.
3. Guiterrez-Osuna, R., Nagle, H. T., Schiffman, S. S., Transient response analysis of an electronic nose using multi-exponential models, *Sen. Actuators B: Chem.*, **61**, 1990, pp. 170-182.
4. Mishra, V.N., Agarwal, R.P., Sensitivity, response and recovery time of SnO2 based thick-film sensor array for H2, CO, CH4 and LPG, *Microelectronics Journal*, **29**, 1998, pp. 861-874.
5. Eklöv, T., Martensson, P., Lundström, I., Enhanced selectivity of MOSFET gas sensors by systematical analysis of transient parameters, *Analytica Chimica Acta*, **353**, 1997, pp. 291-300.
6. Javier G. Monroy, Javier Gonzalez-Jimenez and Jose Luis Blanco, Overcoming the Slow Recovery of MOX Gas Sensors through a System Modeling Approach, *Sensors*, **12**, 2012, pp.

13664-13680.
7. Gardner, J. G., A Non-linear Diffusion-reaction Model of Electrical Conduction in Semiconductor Gas Sensors, *Sen. Actuators B: Chem.*, **1**, 1990, pp.166-170.
8. UST GmbH 2013, priv. communication
9. www.figaro.co.jp
10. HLS-440 Data sheet: http://appliedsensor.com/pdfs/HLS-440_1009.pdf.
11. Lang, M., Banach, U., Nörthemann, K. et al., Long-Term Stability of a MEIS Low Energy Hydrogen Sensor, *Sen. Actuator B: Chem*, 2013 in press, online 11 January 2013.