Project no**.: STRP 017310 SANES**
Project acronym: **SANES**

Project title: **INTEGRATED SELF-ADJUSTING NANO-ELECTRONIC SENSORS**

Instrument: Specific Targeted Research or Innovation Project (STREP)

Thematic Priority NMP-2004-IST-NMP-3

D24 – Publishable final activity report

Period covered: from 01/04/2006 to 31/03/2009 Date of preparation: 21/06/2009

Start date of project: 01/04/2006 Duration: 36 months

Project coordinator name: Dr. Imre Kiricsi
Project coordinator organisation name: University of Szeged Revision: final

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1. Project execution

1.1 Background

Carbon nanotubes demonstrated in the past decade that their exciting electronic and mechanical properties make them one of the most promising materials of the 21st century. The absorption of atoms or molecules on the outer walls of carbon nanotubes can affect their properties, for instance the electrical conductivity of the nanotubes. In this way the nanotubes could act in the long term as sensors to detect (bio)-chemicals in industrial or in medical environments, and proposals of this kind exist in the literature.

Several sensor devices –including carbon nanotube based ones– are already available. However, the works known to be dealing with physical and chemical sensors based on CNTs take the “one factor at a time” approach and suffer from shortcomings such as:

- using large (even macroscopic) amounts of nanotubes to perform a single sensor task
- not using advanced signal processing techniques which would allow a significant reduction in the number of signalling elements
- lack of reliability in carbon nanotube interfacing to MOS processing and control electronics (inadequate contacts, Schottky barriers etc.)
- lack of understanding of the transport phenomena responsible for signal generation and transduction in carbon nanotubes

The future applications of intelligent sensors (in environmental care, automotive, healthcare and in home use) to be developed in the framework of this international collaboration contribute significantly to the improvement of human health and to the protection of nature. It is expected that the target general sensor device can be mass-produced at a very low cost as compared to the specialized sensors applied now. Cost reduction will mainly arise from the fact that only one device must be manufactured instead of several specialized ones. Consequently, consumer product manufacturers will be able to incorporate more sensors into their products (e.g. cars, household appliances etc.) which in turn will allow –because of the increased amount of information available real-time– more advanced artificial intelligence systems and thus lead to a higher quality of human life.

The originality of the SANES concept is that by combining single-molecule nanodevices with the signal processing technology necessary to handle their output, we plan to build a nano-electronic sensor device which is not merely a duplication of existing sensors using a host of nanometer sized elements instead of micrometer sized ones. Rather, the SANES module will be able to detect and process very small signal changes occuring in individual single-molecule carbon nanotube sensor elements. Consequently, it will have a tremendously enhanced measurement capacity as compared to currently available sensor modules. The extra capacity will be used to allow the SANES module to dynamically reconfigure itself in order to provide a full characterization of its environment.

Using the new tool comprising micro and nano patterning and combining it with the molecular building blocks of the single-tube sensor elements it will be possible to study the effects on a few molecule scale which is clearly an advantage to the actual state of the art where the integration over a large number of building blocks is averaging and blurring out the interesting molecular phenomena. The combination of measurement and theoretical modelling has to be highlighted as well and is an inherent part of the interdisciplinary approach used in SANES.

1.2 Project objectives

The general objective of the project is to develop an integrated self-adjusting nanoelectronic sensor (SANES) based on functionalized carbon nanotubes as active elements. The multifunctional sensor micromodule will consist of a matrix of differently functionalized CNTs which are integrated into an electronics package (electronics and software also developed in the framework of the project) capable of:

- recording and analyzing the signal of a very small number of sensing elements
- monitoring several factors (e.g. temperature, pressure, gas atmosphere etc.) simultaneously
- actively change the characteristics of the sensor so that its response can be optimized towards the measurement needs of a changing environment.

The particular novelty of the SANES concept is that the sensor module will be able to dynamically self-adjust its behaviour so that it can meet the changing measurement requirements of its user. This multiplexing behavior will be achieved by integrating the carbon nanotube sensing elements into a matrix which is capable of purposefully and reversibly changing the characteristics of the sensor.

The primary objective of this proposal is to design, construct and analyse such novel sensor modules integrated in an intelligent micromodule. We intend to build a working demonstator of the module and perform its complete evaluation regarding sensitivity, selectivity, stability and reproducibility.

The contemporary sensor market is dominated by low cost semiconductor sensors that usually focus on quantitative measurements and often neglect the importance of chemical selectivity in gas sensing. Therefore, the proposal SANES sensor array having advanced features such as tunability and multifunctionality is indeed a pioneer device in its field of application.

1.3 Methodology

In Figure 1. the block composition plan of the SANES prototype unit is shown. The actually realized prototype differs from this scheme only insofar as it does not use separate nanoactuators, but rather, it utilizes an advanced noise analysis method (Fluctuation Enhanced Sensing) to grant the sensor unit the required multiplexing capabilities.

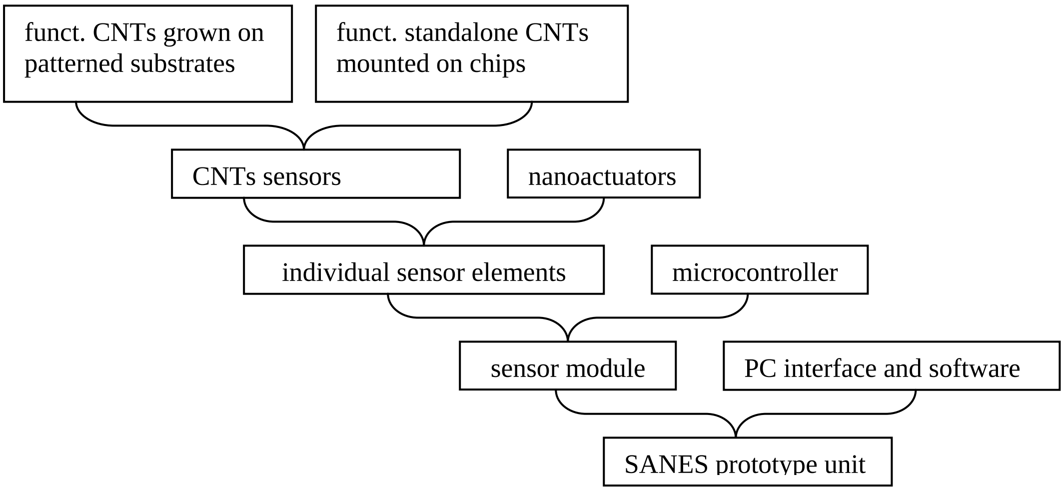
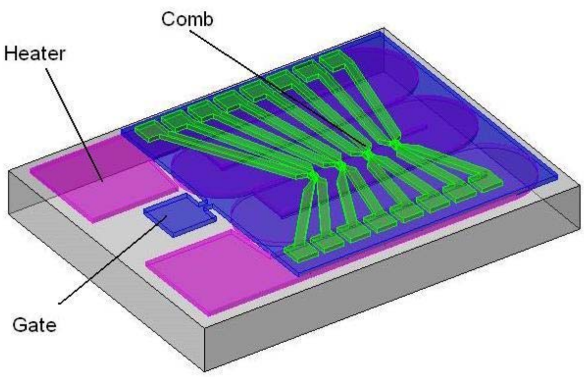


Figure 1. Block composition of the SANES prototype unit



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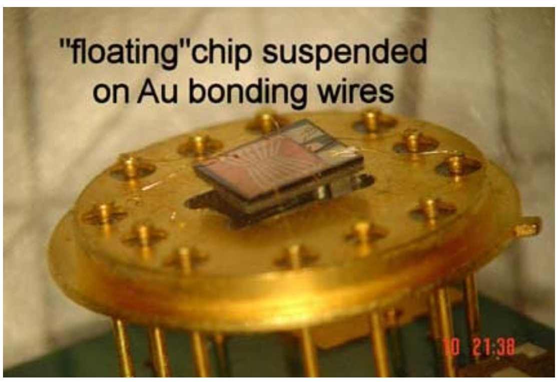

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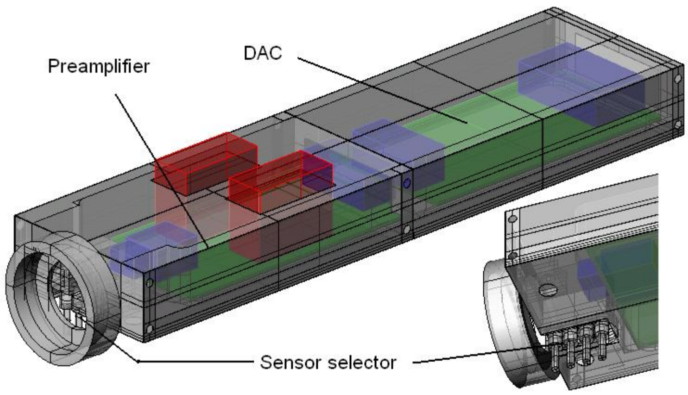

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Figure 2. Assembly stages of the SANES prototype device: A: multilayer chip for four parallel 4-channel measurements, B: multilayer chip with an inkjet printed CNT layer, wire bonded into a TO-8 housing, C: 3D plans of the interface unit consisting of a preamplifier and a data acquisition module, and D: completely assembled prototype test bench.

Concerning the hardware assembly of the unit: the multilayer sensor chip was prepared by litography and carbon nanotubes were deposited on the electrode surfaces by using a high precision inkjet printer (Fig. 2A). The chip was suspended by gold wires in a floating chip arrangement inside a TO-8 package (Fig. 2B). This sensor module is interfaced via special low-noise high precision electronics (Fig. 2C) to a personal computer. In Fig. 2D the assembled test bench with the gas test chamber on the top of the table is shown.

The SANES consortium benefitted a lot from strong theoretical support of the UPV/EHU group. The systems were modeled within the Density Functional Theory (DFT), using the Kohn-Sham approach and treating electron-electron interactions in the framework of the Local Density Approximation (LDA), including corrections from Generalized Gradient Approximations (GGA) when possible and necessary. Depending on the properties we want to calculate, we use plane waves (PW) or localized orbitals (LO) as a basis set. Since all experimental measurements are based on conductance, we have decided to use transmission as an indicator of the changes in the electronic properties of the nanotubes induced by the adsorption of functional molecules. Transmission is a key concept linking the electronic density of states to the transport properties by giving the number of possible conduction paths, i.e. the number of possibilities for an electron to go through the system considered. The conductance is directly obtained from the transmission by multiplying the latter by the quantum of conductance.

The particular novelty of the SANES prototype sensor device is that features an unmatched high chemical selectivity for a broad range of gases. This was achieved by utilizing a novel approach to CNT sensorics that has not been applied prior to the SANES project on a prototype scale. Fluctuation enhanced sensing (FES) is a method based on the fact that the noise of a sensing system – arising from the adsorption/desorption of the analytes on the sensor surface - carries chemical information about the analyte. This means that by analyzing the output data of the sensor with a proper mathematical technique, chemical selectivity can be achieved. The method can also be very sensitive, when using the amplitude of the power spectral densities (PSD) of the sensor's resistance fluctuation, as sensor signal. The final output of the sensor is the so-called Principal Component Analysis (PCA) map of the PSD signal which represents the information contents of the sensor noise in an easily comprehendable graphical format.

1.4 Project achievements with respect to the original project objectives

<u>Excerpt from the 19 October, 2006 version of the SANES Description of Work (page 5, project objectives):</u>

„In this framework we intend to deliver the following verifiable main demonstrators:

- *5 pieces of minimum 1x1 cm patterned substrates containing at least three different types of carbon nanotubes which are in principle able to sense three different parameters (either chemical substances or physical properties like temperature, pressure, electric fields etc.).: 15 months*
- *3 individual board-mounted carbon nanotube based nanosensor devices capable of measuring different physico-chemical properties: 26 months*
- *1 prototype integrated SANES module capable of continuously monitoring at least three different environmental properties and dynamically reconfiguring itself to allocate measuring resources to characterize its environment always at maximum efficiency. The module should communicate with a PC and be able to perform measurements both in supervised and in unsupervised mode: 33 months*

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The final prototypes will be capable of sensing and measuring various gas/vapor-phase chemical substances and their concentration, respectively. The ultimate goal here is to enable simultaneous detection, i.e. measurement of mixtures of chemicals being present in our daily life. Accordingly, the prototype could be suitable for measuring:

- *CO (1-1000 ppm)*
- *CO_2 (1-10000 ppm)*
- *NO_x (1-1000 ppm)*
- *CH_x (1-1000 ppm)*
- *NH_3 (1-1000 ppm)*
- *H_2S (1-100 ppm)*
- *H_2O (1-10000 ppm)*

- *Pressure (10^{-3}-10^{2} bar)*
- *Temperature (77-500 K)*

The dimensions and mass of such a complex sensor module will be a size of a matchbox. In the prototyping phase, the sensor module will be connected to the control unit via specialized cables and communications protocol. The control unit will communicate with a personal computer through standard USB protocol. High-level drivers for accessing the controller will be also developed within the project framework. "

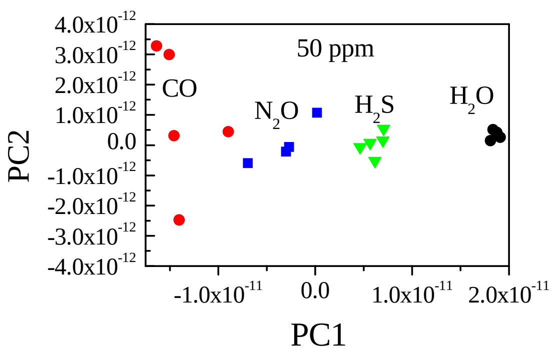
<u>Actual project achievements:</u>

- Several tens of 1x1 cm patterned substrates containing carbon nanotubes were prepared
- Over one hundred pieces of carbon nanotube based nanosensor devices (chips) were prepared by the partners. These devices fall into three major categories: (i) original Oulu design, (ii) MPI-FKF design, (iii) new Oulu design. All these devices were experimented on, and the new Oulu design was selected as the basis of the SANES prototype device.
- One fully functional prototype device was realized. This unit is available for inspection at the University of Oulu. Main features of the prototype device are:
  - the sensor module is located in TO-8 housing, which is much smaller than a matchbox.
  - the sensor module and the control unit are connected, the control unit is approx. the size of two matchboxes
  - the device communicates with a personal computer through USB

- high-level drivers and a fully functional software capable of unsupervised measurement and data analysis were developed and are used in the prototype demonstrator

- The most important goal of SANES was to develop a sensor device with superior multiplexing ability. That is, a device which is able to react to changes in its environment and tune its individual sensor elements in such a way that its chemical selectivity remains high. This was the state of the art in 2004 and on this basis we endeavored to measure three different environmental properties simultaneously.

  Advances in the past five years have allowed the SANES consortium to significantly outperform these original expectations. This is made possible by using Fluctuation Enhanced Sensing (FES). We have proven the by using FES it is possible (i) to use a single sensor to measure four different analytes selectively (Fig. 3A), (ii) to combine selective qualitative analysis with quantitative information collection (Fig. 3B), (iii) to reliably measure gas concentrations that are one order of magnitude smaller (Fig 3C) than those anticipated originally, and to (iv) maintain its performance for at least five months (Fig. 4).



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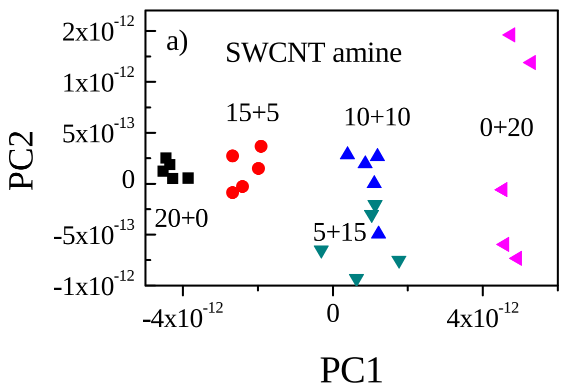

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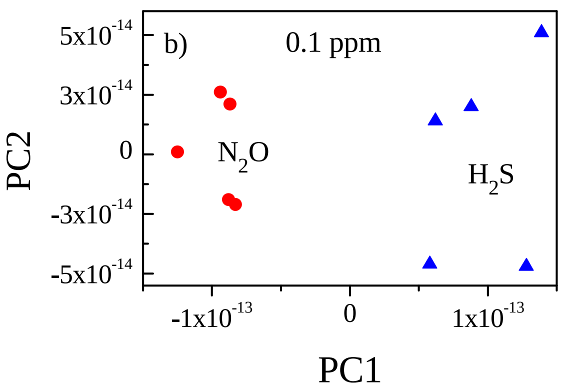

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Figure 3. PCA score maps demonstrating the most important features of the SANES prototype device. A: Clear differentiation between four different gases using the same CNT sensor; B: using a CNT sensor for combined qualitative and quantitative analysis (x+y=20 ppm mixtures of N_2O (x) and H_2S (y)); Reliable chemical selectivity achieved at 0.1 ppm target analyte concentration.

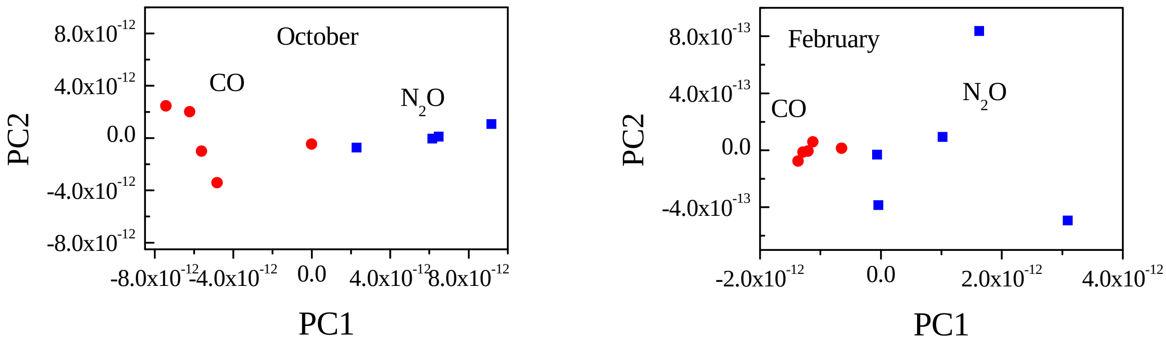


Fig. 4 PCA score maps for exposures of 50 ppm CO (red circle) and N_2O (blue square) for the 1,8 diamino-octan functionalized CNT sensor in October 2007 and in February 2008.

Since the final SANES prototype device is based on the "new Oulu sensor chip" design which uses four independent sensors that are all software-switchable, we may conclude that the SANES prototype is capable of:

- measuring temperature (using the built-in Pt sensor)
- qualitatively differentiating between 16 different gases (4 gases for each sensor) provided that a suitable calibration is available
- quantitatively measuring gas concentrations in the 0.1 ppm … 2000 ppm range

The following milestones were used for reaching the objectives of the project:

M1 (9 months): The objective of the milestone is to determine which patterned substrates should be studied further.

M2 (18 months): The mid term clause corresponds to the decision about which sensor–chemical environment pairs are to be studied further in the detailed sensor testing step. Of all the functionalized CNT–nanoactuator–gas triplets, 5 will be chosen for further experiments.

M3 (28 months): The modules of best reliability and functionality will be chosen to continue with optimization and module testing.

M4 (35 months): The recommended working conditions of a complete SANES unit are to be determined. On this basis, a roadmap for further development/application is to be established.

SANES was a successful project that finished on time and delivered a prototype sensor device which actually surpasses the original project objectives by a factor of five concerning gas selectivity and by an order of magnitude concerning lower detection limit. Perhaps it is even more important to realize that the SANES prototype is the first working device with any mass production prospects which actually uses singe nanotubes as sensing elements. Indeed, each junction between each two

CNT pair functions as a selective adsorption site in the printed CNT film, and Fluctuation Enhanced Sensing made it possible to actually read out this selectivity information from the film.

1.5 Management data

The project was realized through the cooperation of six network partners: three European (University of Szeged, Hungary; University of Oulu, Finland; University of Pais-Vasco, Spain) and one USA university (Rensselaer Polytechnic Institute, USA), one European research institute (Max-Planck Insitut for Solid State Research, Germany) and a European SME (LaserProbe Oy, Finland).

The SANES project ran for 36 months between 1st April 2006 and 31st March 2009. The direct project effort amounted to 301 person months + 184 AC person months, distributed into 9 work packages. The actual project budget used was 1315844 EUR. The requested financial contribution of the European Commission amounted to 1201500 EUR.

2. Dissemination and use

Considerable effort has been devoted to knowledge dissemination and exploitation activities. The final Plan for Using and Dissemination of Knowledge (PUDK) is a 90 page long document on its own, discussing the details of these activities.

2.1 Knowledge dissemination activities of the SANES consortium

The main workhorses of knowledge dissemination in SANES were two dedicated workshops (SIWAN 2007 and SIWAN 2008), the scientific publications (over 50) and the invited conference talks (over 10) authored by the SANES partners. A summary of these activities is presented below.

Planned/actual Dates (*)	**Type**	**Type of audience**	**Countries addressed**	**Size of audience**	**Partner responsible /involved**
2/2	Press release	General public	Hungary	350000	SZTE
8/10	Project web-site	General public	English speaking world	Over 1 million	SZTE
continuous	Publications (more than 50 papers in peer-reviewed journals)	Research	English speaking world	Over 1 million	Home institute of the corresponding author
19/19	Workshop SIWAN 2007	Chemists, physicists, material scientists	Hungary, Finland, Spain, USA, Switzerland	100	SZTE (organizer) + all partners (presenters)
–/28	Project introduction in the journal Nanopages	Chemists, physicists, material scientists	English speaking world	10000	SZTE
-/29	Project introduction at SPIE Optics+Photonics 2008, San Diego USA as an invited talk	Chemists, physicists, material scientists	Optics, physics and materials science community	1200	SZTE
31/31	Workshop SIWAN 2008	Chemists, physicists, material scientists	Hungary, Finland, Spain, USA, Switzerland	150	SZTE (organizer) + all partners (presenters)
-/39	Project introduction at E-MRS 2009,	Chemists, physicists, material	Optics, physics and	1100	SZTE

Planned/actual Dates (*)	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
	Strasbourg, France as an invited talk	scientists	materials science community		
Continuous	Project presentation in local media	General public	Local communities	500000	SZTE, UPV, Uoulu, MPI

2.2 Exploitable results

Ten different potentially exploitable results have been identified by the consortium at a dedicated Exploitation Strategies Seminar. These are:

Result n°1 “Nanopaterned substrates” (product)

Result n°2 “Ink-jet printing” (method)

Result n°3 “CNT based sensors (product)”

Result n°4 “Electronics” (know-how and product)

Result n°5 “Sensor design and modelling simulations” (know-how)

Result n°6 “Microcontroller (software)”

Result n°7 “Fluctuation enhanced sensing (FES) (for specific gases)” (know-how and product)

Result n°8 “Sensor module” (product)

Result n°9 “SANES unit” (product)

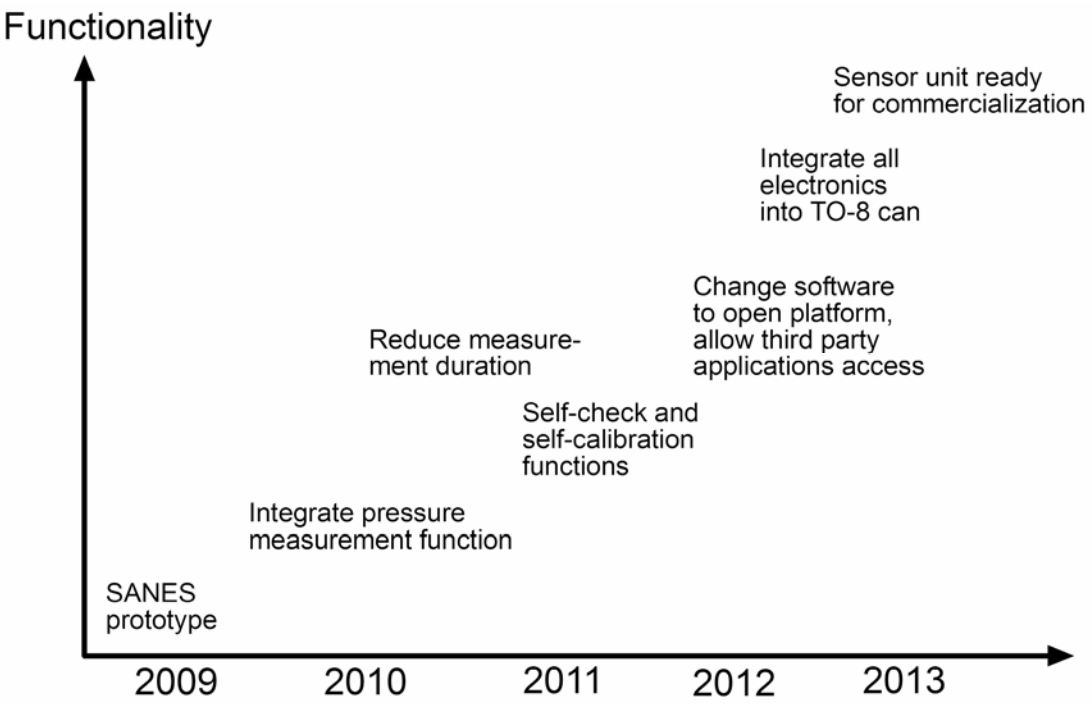
Result n°10 “Training material” (product)

All of these ten results were examined in detail with respect to their contents, their Intellectual Property Rights situation and exploitation risks in the PUDK. Exploitation options including purchasing and licensing rights are open to interested third parties, who should contact the project manager (Dr. Ákos Kukovecz) for more information.

2.3 Development options

In the framework of the SANES project we developed a complete gas sensing prototype unit with very high selectivity. Since the sensor market today is flooded with cheap semiconductor sensors capable of measuring single analytes, we believe that the best business opprtunity for the commercialization of a SANES device is to aim at niche markets demanding high selectivity, sensor versatility and dynamic sensor reconfigutation possibilities.

Presuming a similar level of financial support intensity, the SANES consortium would be able to develop the device into a marketable end-product within 4-5 years by following this roadmap:



3. Contact information

The SANES project was coordinated by Prof. Dr. Imre Kiricsi, Head of Department of the Dept. of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary. The evolution of the project can be monitored on the project homepage: http://www.sanes.u-szeged.hu/

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