

System for European Water Monitoring (SEWING)

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Abstract

In the European Union 5th Framework Programme the project SEWING (System for European Water monitorING) was done in the years 2001-2004. Its objective was to create a flexible, easy accessible on-line system for measuring water pollution with non-organic ions in real time. To reach this objective many interdisciplinary R&D actions were to be done: in the field of electronics - semiconductor sensors, in the field of chemistry - these sensors had to be done selective for selected ions, in the field of computer science - software for data extracting and finally in the field of micro-mechanics - the automatically controlled hydraulic system. These works were concluded with success, constructing a prototype of the system, which was thoroughly examined by the representative of the end-users. This prototype creates a basis for further works having as the aim industrialisation of the system and being ready for market production of not expensive, universal and flexible system, which is user-friendly and can be easily exploited.

1. Introduction

In December 2004 a 3-years FP5 European Project SEWING has been finished with success. The objective of the project, formulated in the contract, was:

Creating a cheap, flexible and generally accessible system for water monitoring against pollution with non-organic ions.

Nine partners from 7 European countries took part in the project:

1. Politechnika Warszawska (PW), Warsaw, Poland – co-ordinator
2. Institute of Electron Technology (ITE), Warsaw, Poland
3. Technical University of Lodz (TUL), Lodz, Poland
4. Valtion Teknillinen Tutkimuskeskus (VTT), Espoo, Finland
5. Centre National de la Recherche Scientifique (LAAS –CNRS) Toulouse, France
6. MICROSENS S.A., Neuchatel, Switzerland
7. Universitat Polytechnica de Catalunya (UPC), Barcelona, Spain
8. Universität für Bodenkultur, Wien, (BOKU). Austria
9. SYSTEA, Rome, Italy

The project was interdisciplinary, combining electronics, information technology, chemistry, environmental engineering, micro-mechanics and semiconductor technology.

This research area had been found important, as the deficit of clean water becomes more of a problem in Europe, and there is a need to develop easily accessible, cheap and reliable Microsystems, which could be used for water pollution monitoring and early warning of many European water resources. The equipment available so far is mostly of laboratory type and measures inserted water samples. The objective of this project was to create a system of continuous water pollution monitoring in real time. Portable equipment has

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been developed, which, when taking automatically samples from water resources, collects data about pollution.

The following four main activities were carried on in order to reach the final aim and will be presented in more details in the paper:

1. Fabricating the CHEMFET sensors selective for particular ions, their measurements, characterisation and verification.
2. Creating mathematical models of these sensors and on that basis creating software for processing of measurement data, including estimation of ion activities in water samples,
3. Building components of the measurement system: computer controlled hydraulics, data acquisition and on-line data processing, remote communication,
4. Final measurements and verification of the system by the representative of end-users.

2. Sensors realisation

One of the most important tasks of the project was the development and construction of ion-sensitive sensors, suitable for the detection of selected choice of non-organic polluting ions, having the requested range of selectivity and sensitivity for water resources and waste water, in high-risk industrial regions. Solid-state electrochemical microsensors based on ISFETs (Ion-Selective Field Effect Transistors) have been chosen to construct the monitoring system. ISFET is a FET, in which the gate field is open for contact with measured water sample. Two kinds of ISFETs were elaborated: Back-Side-Contact (BSC) and Front-Side-Contact (FSC), their use depends on the technical and economical requirements of the final system. Finally BSC sensors were used in the prototype. A standard ISFET structure with a pH-sensitive silicon oxide/silicon nitride ($\text{SiO}_2/\text{Si}_3\text{N}_4$) gate structure was developed using silicon technology. After covering the gate field with an ion-selective polymeric membrane, containing an appropriate ionophore, these generic pH-ISFETs are transformed into CHEMFETs, that means CHEMICally modified Field Effect Transistors.

Sensors selectively sensitive for the following ions were developed during the project: NO_3^- , NH_4^+ , K^+ , Na^+ , and additionally for H^+ (pH). The constructed CHEMFETs were based on different ion-selective polymeric membranes, and on different ways of deposition. They were studied and compared for the mass deposition of ion-sensitive layers according to industrial requirements. Their life-time is at least 3 months; their reproducibility, performance, and selectivity fulfil the technical requirements. The range of sensitivity is according to European standards for surface and drinking water.

Several steps had to be followed in order to obtain CHEMFETs with desired properties.

- Fabrication of back-side contact BSC-ISFETs (ITE) – used in the final prototype
- Fabrication of front-side contact FSC-ISFETs (LAAS-CNRS)
- Characterization of pH sensitive ISFETs
- Industrial deposition of the polyHEMA on ISFETs
- Optimization of the final composition of ion-sensitive membranes (polymer materials: PVC and polysiloxane) (Politechnika Warszawska -PW- Poland)
- Deposition of NO_3^- , NH_4^+ , K^+ , Na^+ ion-sensitive membranes – realisation of CHEMFETs.

2.1 Fabrication of back-side contact BSC-ISFETs (ITE) and front-side contact FSC-ISFETs (LAAS-CNRS)

Back-Side-Contact (BSC) and Front-Side-Contact (FSC) ISFETs were respectively fabricated in the Institute of Electron Technology (ITE), Poland, and in the Laboratory of Analysis and Architecture of Systems, (LAAS) France. They have source and drain contacts on the bottom of the chip, while on the upper side the

open gate is available. Figures 1 and 2 show the drawing of cross section of the BSC ISFET and the FSC ISFET respectively.

2.2 Deposition of polymer layers

In order to obtain reproducible CHEMFETs there was a need to deposit intermediate layer between gate and final ion-sensitive membrane. This intermediate layer, based on poly(2-hydroxyethyl methacrylate) (poly-HEMA), plays role of buffered solid electrolyte in electrochemical sensors. Industrial deposition of the polyHEMA layer on ISFETs has been done in Institute of Electron Technology in Warsaw applying spin-coating technique and radical, in situ polymerization.

Ion-sensitive membranes selective for NO_3^- , NH_4^+ , K^+ , Na^+ , based on two polymeric matrices: plasticized poly(vinylchloride) (PVC) and polysiloxane (PSX), were carefully optimized in PW. Membranes of optimised composition have been deposited applying standard photolithographic process (for FSC, figure 3-a) and automated dispensing unit (for BSC, figure3b). The unit allows depositing 5 microliter volume of the solution of polymeric membrane with high reproducibility.

2.3 Characterisation of CHEMFETs

It took many months to get finally the BSC CHEMFETs with good properties. These properties are the following:

- Reasonable production yield,
- Expected sensitivity and selectivity for selected ions,
- Life-time of at least 3 months,
- Time drift in reasonable limits, allowing automatic calibration before each measurement.

Exemplary responses of CHEMFETs selective for NH_4^+ ions and NO_3^- ions (figure 4) are presented below.

Table 1 shows performances of the final CHEMFETs designed and fabricated in PW in collaboration with ITE.

Table 1.
Performances of ion-selective CHEMFETs

	Measuring range [mg/l]	Long-term stability
pH	2 – 12 pH	~ 1 year
K^+	2 – 3 900	at least 3 months
Na^+	2.3 – 2 300	
NH_4^+	1.8 – 1 800	
NO_3^-	6 – 6 000	

3. Mathematical models of sensors and software for data processing

Sensor modelling had several goals in mind. Models are very useful, when designing measurement setup circuitry. Model characterisation allows for comparison of devices from different manufacturing batches and estimation of variability. Finally, models have to be used in measurement data processing software, that is to compensate for sensor non-idealities.

Most of the models, that have been considered in SEWING research, assumed separability of the CHEMFET two-domain (electrical-chemical) device model into two parts: chemical and electrical.

Three main versions of the chemical sub-model have been considered for CHEMFETs:

- Nikolski-Eisenmann (NE) model – standard, semi-empirical, limited in accuracy,
- Van den Berg (VDB) model – physics based, complicated, implicit, but accurate,
- Super-Nikolski-Eisenmann (SNE) model – simplified VDB, physics based but still simple (created by PW) (Ogrodzki 2002, Ogrodzki 2003, Ogrodzki 2004).

The electrical sub-models were adaptations of known FET models for circuit simulation programmes. The models were specially tailored for the needs of accurate modelling of particular silicon structures used for the SEWING project (e.g. depletion mode FETs from ITE).

Mathematical models and appropriate automatic characterisation software (CEDaR) have demonstrated possibility of pretty accurate prediction of CHEMFET behaviour in wide range of conditions: electrical (operating point), chemical (ion concentration in the sample) and environmental (temperature). Fig. 5 presents an exemplary comparison of CHEMFET measurements (dotted curves) and model responses (solid lines) for 3 temperatures (10, 20 and 30 centigrades) for very wide biasing range of the sensor.

Validation of CHEMFET models and parameter extraction software enabled design of an on-line data processing software for the final SEWING demonstrator (Filipkowski 2003).

Three different measurement data processing methods were created in the framework of the SEWING project. They were called, respectively:

- Data Fusion (DF, created by PW) (Opalski 2002),
- Inverse modelling Problem Algorithm (IPA, created by TUL),
- Blind Source Separation of stochastic responses of an array of sensors (BSS created by UPC).

The first one has been used in the prototype and is described below.

The general principle of Data Fusion (DF) algorithm is shown in fig 6. DF combines “raw” information from several sensors of limited selectivity (could be even of different type), taking into account accurate models of non-ideal sensors, so as to improve on quality of output data (e.g. ion estimation accuracy).

The DF principles were used for design of an on-line data processing software that was embedded in the final SEWING principle. To reduce influence of sensor drift and to reduce so called matrix effects, i.e. influence of interfering ions that are not directly measured in the sensor matrix - multiple standard addition measurement scenario was implemented (Fig. 6b). Water sample is now stored in the measurement chamber (reactor), and pre-treated with an Ionic Strength Adjuster (ISA). After that, read-outs from all sensors are stored in memory. Then a precisely controlled amount of a standard solution (containing precisely controlled type and concentration of selected ions) is injected into the reactor and the read-outs from all sensors stored again. Injections can be repeated with the same or different standard solutions. The DF algorithm based on sensors models is implemented in the firmware of the system and extracts the data about concentration of particular ions, taking into account interference matrix and temperature.

4. Technological realisation of the prototype

All elements of the system were verified in successive approaches of the prototype. The first one was the LFA (Loop Flow Analysis) unit build by SYSTEa, very flexible equipment, in which all elements could be checked in working conditions and adjusted for best performance. It is shown in fig 7.

All the parameters can be easily changed on the key-board and the results are printed by the internal printer. Digital display allows controlling the measurement process.

Finally it was decided that a different, more flexible prototype is constructed (by SYSTEVA), called Micro-Mac-1000, shown in fig 8. The following are the main properties of the prototype:

- Portable/on-line, multisensors measuring device, with intrinsic automatic calibration capability,
- possibility of integration of both type of BSC and FSC Chemfet sensors, extensively tested by BOKU partner,
- possibility of integration up to eight different sensors in the flow-cell.

When building the prototype integration of PW DF calculation algorithm and development of a new dedicated PC remote interface program was done. In that way the results of water sample measurements can be visualised.

The most expensive part of the prototype is the programmed hydraulic system, which performs the following activities:

- calibrating the sensors with standard sample,
- introducing the measured sample,
- introducing samples according to standard addition method,
- washing the sensors and embedding them in standard liquid.

The sensors are inserted in a specially designed flow-cell, where reference electrode and temperature sensors are also inserted. The prototype described above gives the starting point for future works leading to industrial implementation of the system.

5. Final measurements and verification of the system

Final measurements were done by the Austrian partner BOKU. The following properties were checked:

- System stability by means of calibration slope
- Limit of Quantification (LOQ)
- Accuracy & Precision by means of control samples
- Accuracy by means of real samples (comparison with reference methods)
- Sensor conditioning time
- Sensor life time and homogeneity.

Preliminary measurements were done on the LFA unit, while the last, most important, on the prototype. Emphasis was put on the sensors behaviour, particularly comparison was done between different technologies and chemical versions of ion-selective membranes.

Figs 9 and 10 show the final accuracy measurements. The equation on the top of each diagram shows the offset (should be zero) and slope accuracy (should be 1).

In the present state, results for drinking and surface water are highly satisfactory.

6. Conclusions

To conclude, the main objectives of the project were met. The vision of the system was rather ambitious and loaded with quite a large risk. So, some deviations from the previously assumed properties of the system occurred. These were:

- The final prototype is not as small as expected. The micro-probe version was constructed, but it occurred difficult to make experiments on it in a flexible way. The idea of smaller instrument is still alive and will be used in industrialisation phase.
- The prototype is not as cheap as expected. It occurred that CHEMFET sensors, to work properly, need to be calibrated and standard addition method should be used, so the hydraulic system is quite sophisticated and raised the cost.

- Only 4 ions are finally monitored, the fifth is in development phase. Preparation of selective membranes occurred quite difficult. Further research in this area is expected. Even with these limitations the prototype occurred very useful.

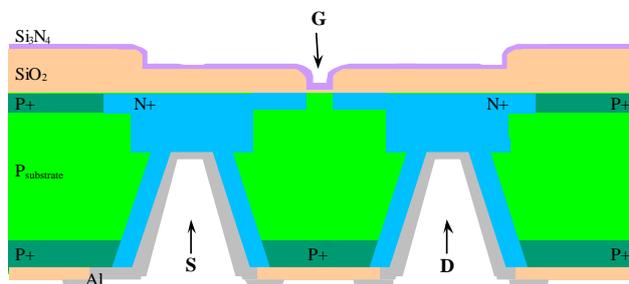


Fig. 1: Cross section of Back-Side-Contact ISFET

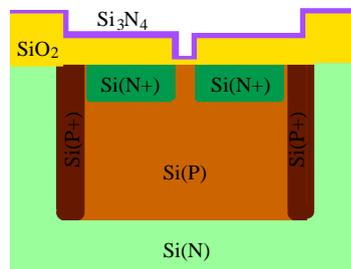
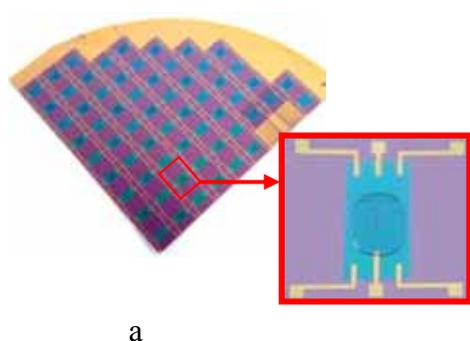
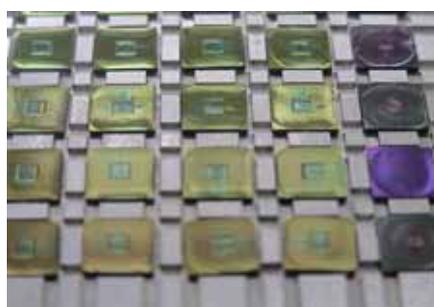


Fig. 2: Cross section of Front-Side-Contact ISFET



a



b

Fig. 3: Ion-selective membranes deposited on ISFETs

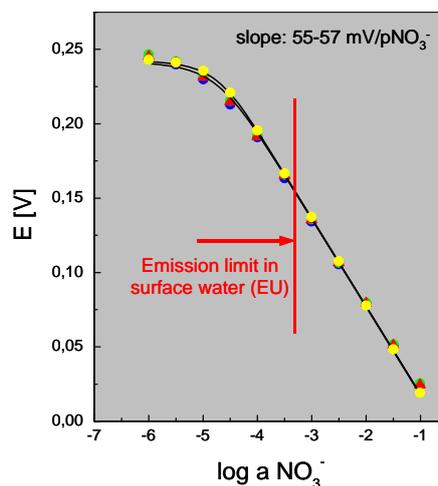
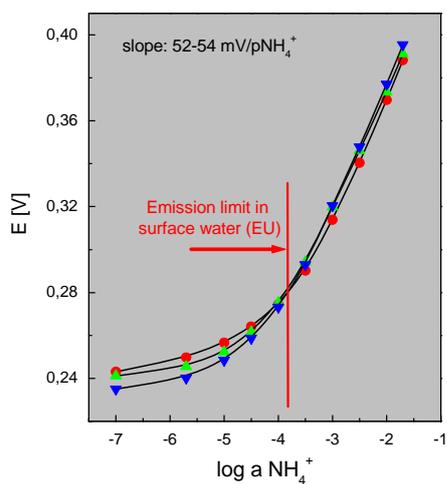


Fig. 4: Responses of NH₄⁺-selective and NO₃⁻-selective CHEMFETs (for several samples)

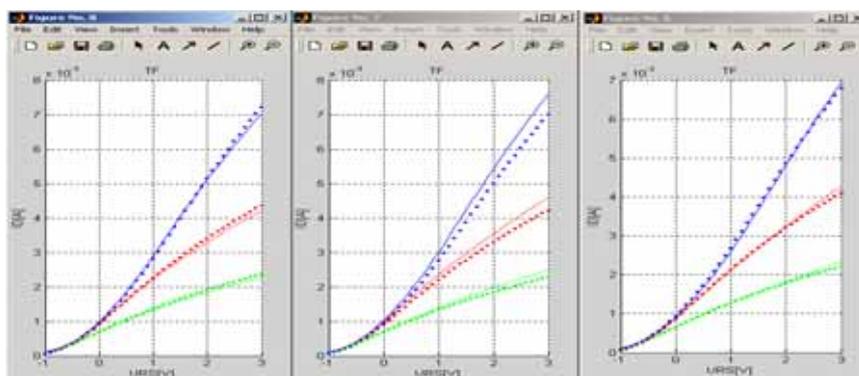


Fig. 5: Comparison of calculated (from models) and measured properties of sensors

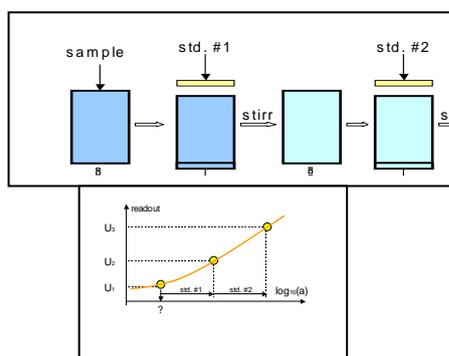
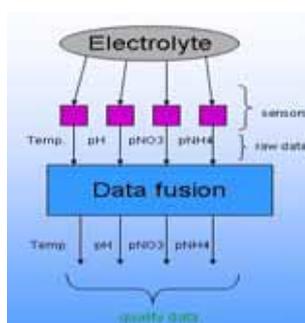


Fig. 6a: Principles of Data Fusion (DF) algorithm

Fig. 6b: Principles of the multiple standard addition procedure



Fig.7: The LFA unit



Fig. 8: The Micro-Mac-1000 unit

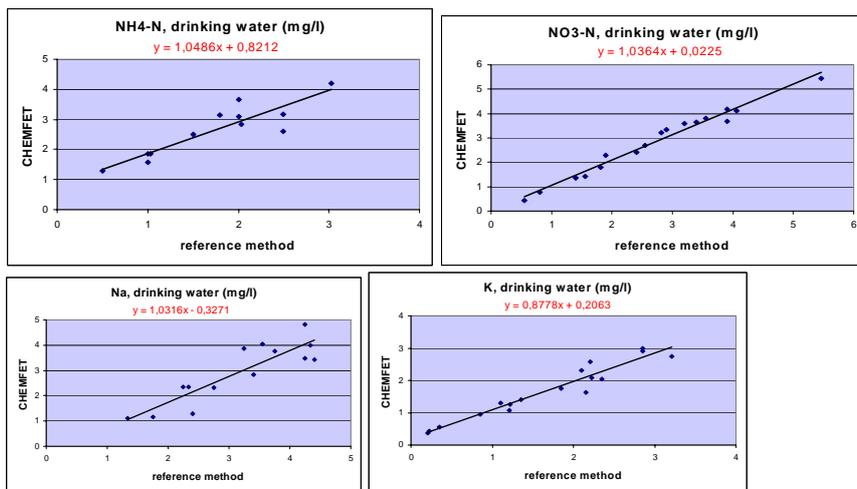


Fig. 9: Drinking Water measurement

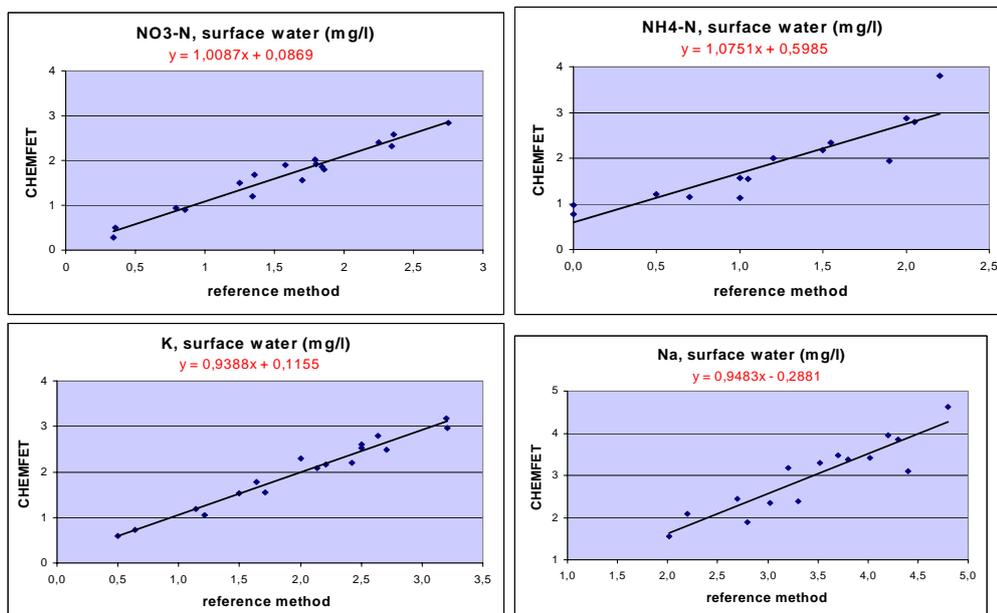


Fig. 10: Surface Water measurement

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