

PIEZORESISTIVE CHEMICAL SENSORS BASED ON THE SWELLING BEHAVIOR OF POLYMERS

M. Guenther^a, G. Suchanek^a, Phan L.P. Hoa^a, J. Sorber^a, G. Gerlach^a, K.-F. Arndt^b

^aInstitute for Solid-State Electronics, ^bInstitute of Physical Chemistry and Electrochemistry, Technische Universität Dresden, Helmholtzstr. 10, 01062 Dresden, Germany

The purpose of chemical sensors consists in converting chemical input data into output signals suitable for electronic measuring processes. The sensors consist of a material-recognizing element and a transducer. We use hydrogel thin films as sensing elements. Hydrogels are cross-linked polymers which swell in solvents to appreciable extent. The amount of solvent uptake depends on the polymer structure, and can be made responsive to environmental factors, such as solvent composition, pH value, temperature, electrical voltage etc. Hydrogels are capable to convert reversibly chemical energy into mechanical energy and therefore they can be used as sensitive material for appropriate sensors. The transducer of our chemical sensors comprises a piezoresistive silicon pressure sensor. It converts the non-electric measuring value into an electrical signal. Therefore, the measurement uncertainty of the transducer is of great concern.

During the last ten years, the "Guide to the Expression of Uncertainty in Measurement" (GUM) [1] has been recognized worldwide for the evaluation and expression of measurement uncertainty. This paper presents a systematic, practical and versatile approach for determining the measurement uncertainties of piezoresistive sensors. The processes of uncertainty evaluation in accordance with the ISO GUM are shown in Fig. 1. The important points of the GUM procedure are the knowledge-based description of the measurement, the evaluation of the input quantities involved by means of probability distributions, and the establishing of the measurement model. This modelling of the measurement process is the most difficult step of uncertainty evaluation. In this work, a transfer model for uncertainty evaluation related to semiconductor piezoresistive sensors is developed (Fig. 2).

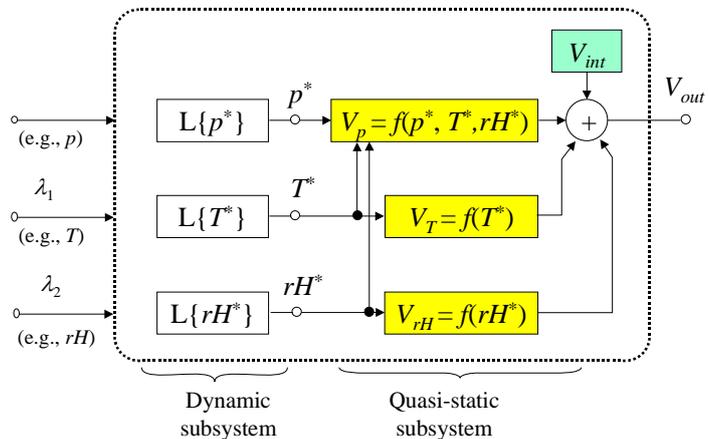
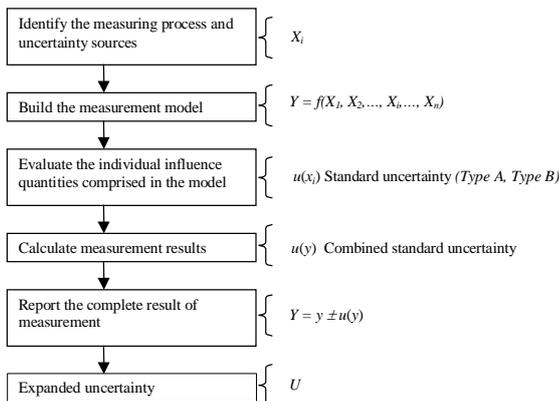
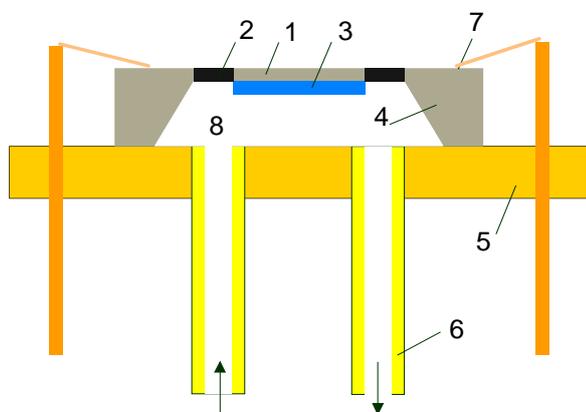


Figure 1. Uncertainty determination steps based on ISO GUM. **Figure 2.** Signal model for pressure sensors.

Instead of separating the quasi-static subsystem to systematic and stochastic parts like in the formal heuristic approach [2], this improved model considers a combined standard uncertainty of the measurement result. In order to explore the measurement uncertainties created when using piezoresistive pressure sensors for data acquisition in an environment of changing ambient or media

conditions, experiments are performed to observe the response of different piezoresistive pressure sensors under appropriate conditions of temperature, humidity, and pressure stimulation. For piezoresistive pressure sensors, it is found that for typical output voltage values of about (10...100) mV, the normalised covered uncertainty amounts to (0.06...0.60)%. Beside temperature, which is usually the dominating contribution to the measurement uncertainty of piezoresistive pressure sensor and which can be widely compensated, humidity plays also a considerable role.

Commercially available pressure sensor chips (Aktiv Sensor GmbH, Stahnsdorf, Germany) were used as mechano-electrical transducers for the transformation of membrane deflections into an appropriate electrical output signal. The hydrogel itself was brought into a cavity at the backside of the silicon chip and closed with a cover. This cavity on the backside of the chip was wet etched with a silicon nitride mask as etch resist. Therefore, only the backside of the chip comes in contact with the measuring species, whereas the frontside with the electronic components is strictly protected from it. Since the sensor chips showed excellent stable properties, the long-term stability of the sensor was solely determined by the stability of the hydrogel characteristics. Figure 3 illustrates the



operational principle of hydrogel-based sensors. The swelling or shrinking processes of the hydrogel were monitored by corresponding changes in the piezo-resistance of an integrated Wheatstone bridge inside a rectangular silicon membrane.

Figure 3: Operational principle of hydrogel-based sensors with PVA/PAA layer, deposited onto the bending plate

- 1 bending plate; 2 mechano-electrical transducer (piezo-resistive bridge); 3 swellable hydrogel; 4 Si-chip; 5 socket; 6 tube; 7 interconnect; 8 solution.

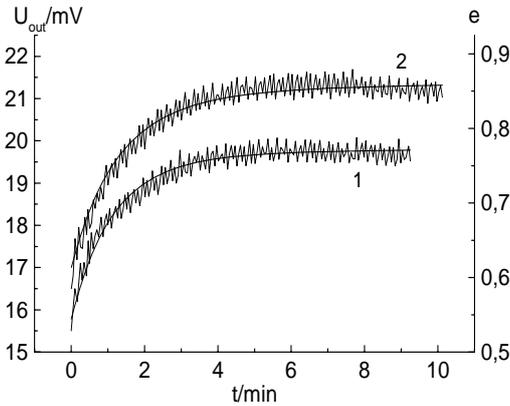
The swelling ability of pH-sensitive hydrogels depends on the functional acidic or basic groups at the polymer backbone. Due to the dissociation of these groups and the influx of counterions, the concentration of ions in the hydrogel is higher than in the surrounding solution. This causes a difference in osmotic pressure and results in a solution flux into the hydrogel and, consequently, in a swelling. The interaction and repulsion of charges along the polymer chain also lead to an increased swelling. The mechanical quasi-equilibrium of ionic gels occurs when the elastic restoring force of the polymer network balances the osmotic forces. During the swelling process hydroxide ions are transported into the neutral gel, while during the shrinkage protons diffuse into the gel and neutralize the negative charged acidic carboxylate groups. This ion diffusional flux induces an electrical potential difference that drives the electromigration of the ions in the direction opposite to that of the diffusion. In so-called "Donnan quasi-equilibrium" the diffusional flux of the ions in one direction is equal to the electromigrational flux in the opposite direction, resulting in a net zero mass transport and a net zero charge transport. A Nernst-Planck equation coupled with the Poisson equation and the mechanical equilibrium equations are used to describe the gel swelling/deswelling process. The change of the electrical potential $\Delta\Psi$ at the gel-solution interface is a function of the pH value of the surrounding solution. Therefore, the gel deformation at different pH values of the solution can be considered as a mechano-electric effect using the linear irreversible thermodynamic modeling and the model of electromechanical coupling in ionic polymer materials.

The total time-dependent deformation e during the hydrogel swelling consists of the deformation e_w , which describes the water flux due to osmotic pressure, and of the deformation e_l ,

which is caused by hydrated ions flux due to their diffusion and electromigration [3]:

$$e = e_w + e_I = e_w + \sum_i \left[d^2 (dc_i / dy)_{t=0} (1 - \exp(-t / \tau_i)) \right] - \sum_i z_i \mu_{i,eff} c_i (\Delta\Psi / d) t \quad (1)$$

where d is the hydrogel layer thickness, $\tau_i = d^2 / D_{i,eff}$ the time constant, $D_{i,eff}$ the effective diffusion coefficient, $\mu_{i,eff}$ the effective mobility, c_i the concentration, and z_i the valence of the i^{th} ion. Figure 4 shows the values of the sensor's output signal and the correspondent calculated values



of the gel deformation for two initial swelling states of the hydrogel. The change of the previous gel swelling state leads to a shift of the corresponding dependence $\Delta\Psi = f(pH)$ and to a change in the time dependence of the deformation in accordance with Eq. 1.

Figure 4: Sensor output voltage U_{out} and calculated gel deformation e during the swelling process from pH1 to pH4.5

1 after initial conditioning in de-ionized water;
2 after initial conditioning in de-ionized water and subsequent exposition in the solution with high pH value.

We have demonstrated the operational principle of piezoresistive chemical sensors based on the swelling behavior of polymers and hydrogels. In a first step, the measurement uncertainty of the applied transducer was analyzed to establish the limits of the operational principle. In order to realize pH sensors, poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA) blend with a pH value dependant swelling behavior was used as chemo-mechanical transducer. The hydrogel swelling leads to a bending of the thin silicon membrane of the pressure sensor chip and, by this, to an electrical output voltage of the sensor. Because the gel response is typically diffusion driven, the time response of the volume change approximately follows the square of the sample dimension. Scaling to micro-dimensions enhances the time response. Consequently, a reduction of the sample size improves the sensor performance. Time constants down to a few ten seconds have been found for thin hydrogel films directly deposited on the membrane backside. The influence of the gel swelling/deswelling kinetics on the response time and long-term signal stability of the proposed pH sensors was investigated.

It was found that an initial conditioning in de-ionized water and the use of the pH sensor only in the dynamic range of the gel volume phase transition at $2.5 < \text{pH} < 4.5$ are conditions necessary for high signal reproducibility. Measurements in solutions with $\text{pH} < 2.5$ and large pH changes should be avoided in order to maintain a sufficient sensor sensitivity for a long time.

References

- [1] Guide to the Expression of Uncertainty in Measurement. 1st ed. International Organization for Standardization, Geneva, Switzerland, 103 (1995).
- [2] A. Lenk. Heuristische Fehlermodelle für Messgeräte. Studie Meßwerterfassung 3/89, Sektion Informationstechnik, Dresden University of Technology, Dresden, 114 (1989).
- [3] M. Guenther, G. Gerlach, J. Sorber, G. Suchaneck, K.-F. Arndt, A. Richter. In: Smart structures and materials: electroactive polymer actuators and devices/ Ed. Y. Bar-Cohen, Proc. SPIE, San Diego, CA, USA, **5759**, 540 (2005).