**Dieses Dokument ist eine Zweitveröffentlichung (Verlagsversion) /
This is a self-archiving document (published version):**

C. Bellmann, A. Steinke, T. Frank, G. Gerlach

Humidity micro switch based on humidity-sensitive polymers

Erstveröffentlichung in / First published in:

SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring.
San Diego, 2015. Bellingham: SPIE, Vol. 9430 [Zugriff am: 02.05.2019].

DOI: <https://doi.org/10.1117/12.2084179>

Diese Version ist verfügbar / This version is available on:

<https://nbn-resolving.org/urn:nbn:de:bsz:14-qucosa2-350301>

„Dieser Beitrag ist mit Zustimmung des Rechteinhabers aufgrund einer (DFGgeförderten) Allianz- bzw. Nationallizenz frei zugänglich.“

This publication is openly accessible with the permission of the copyright owner. The permission is granted within a nationwide license, supported by the German Research Foundation (abbr. in German DFG).

www.nationallizenzen.de/

PROCEEDINGS OF SPIE

[SPIDigitalLibrary.org/conference-proceedings-of-spie](https://www.spiedigitallibrary.org/conference-proceedings-of-spie)

Humidity micro switch based on humidity-sensitive polymers

C. Bellmann, A. Steinke, T. Frank, G. Gerlach

C. Bellmann, A. Steinke, T. Frank, G. Gerlach, "Humidity micro switch based on humidity-sensitive polymers," Proc. SPIE 9430, Electroactive Polymer Actuators and Devices (EAPAD) 2015, 94302F (1 April 2015); doi: 10.1117/12.2084179

SPIE.

Event: SPIE Smart Structures and Materials + Nondestructive Evaluation and Health Monitoring, 2015, San Diego, California, United States

Humidity micro switch based on humidity-sensitive polymers

C. Bellmann^{*a}, A. Steinke^b, T. Frank^b, G. Gerlach^a

^aTechnische Universität Dresden, Laboratory of Solid-State Electronics; D-01069 Dresden, Germany

^bCIS Forschungsinstitut für Mikrosensorik und Photovoltaik GmbH, Erfurt, Germany

ABSTRACT

We present recent results on a binary threshold sensor based on the binary zero-power sensor (BIZEPS) platform which is able to use the energy provided directly from the measured relative humidity of the ambient air to mechanically switch an electrical micro contact. This zero-power switch behavior is realized by using the humidity-sensitive volume swelling of a polymer layer as the detection element deflecting a mechanically deformable silicon boss structure, thus closing the electrical contacts of the switch. For the humidity-sensitive sensor switch considered here, a humidity-sensitive hydrogel blend of poly(vinyl alcohol) and poly(acrylic acid) was used. The sensitive part affected by the measurand is completely separated from the electrical part, thus providing long-term stability. By using an inverse silicone stamping technique the polymer layer with a thickness of about 15 μm was patterned on test structures possessing a thin silicon flexure plate of 5 mm x 5 mm in size and 20 μm in thickness. Reproducible deformations of up to 15 ... 24 μm has been measured. Investigations of the swelling kinetics showed for several discrete relative humidity values a saturation of the water load. The time to reach this saturation state is reduced from 5 hours down to approx. 20 min by increasing the relative humidity beyond the threshold value of 70% r.H. A significant influence of the temperature to the humidity load could not be observed.

Keywords: binary sensor switch, relative humidity, zero-power, boss structure, hydrogel, PVA-PAA

1. INTRODUCTION

Remarkably, 70% of all sensors in process control and more than 90% in building automation are sensor switches acting as threshold switches when changes of particular conditions require dedicated actions [1]. For these purposes sensors are required which switch between two predefined states. Most of the commercial sensors related to this task are based either on a resistive, a capacitive or an optical measurement principle [2] [3]. Unfavorably, they need an electrical processing circuitry as well as an external energy supply during the entire operation time to monitor the desired parameter continuously (Figure 1).

Figure 1: a) State-of-the-art sensor system requiring steady energy supply and b) sensor system based on the BIZEPS platform without energy supply for switching

This paper describes an approach for the two-point control of relative humidity and the reduction of system complexity (figures 1). In [1] we proposed a binary zero-power sensor (BIZEPS) where the humidity leads to a swelling of a humidity-sensitive hydrogel as the transducer element [4]. In contrast to existing solutions, this swelling provides the energy to trigger mechanically an electrical contact. As long as a defined threshold is not reached, the electrical micro contact remains open. Only after passing the threshold value the switch will be triggered and hence the contacts will be closed without any electrical power supply. Advantages of such polymers are their easy processing technology, their low cost, the adequate availability and the possibility to tailor their properties. The effect of polymer swelling is already used in bimorph sensors [5], biosensors [6] and in sensors for reflectometric interference spectroscopy [7].

Figure 2: Principle configuration of the BIZEPS platform

For our purpose two swelling mechanisms can be used [8]:

- The first mechanism uses the volume increase of the polymer. Due to the absorption of water molecules the polymer becomes almost incompressible. The restriction of the free space results in a high swelling pressure.
- The second approach uses the principle of the bimorph effect which is based on two connected material layers with different linear expansion coefficients. In dependence on the targeted measurand, e. g. relative humidity, this leads to a bending of the layer system in a certain direction.

The mechanical BIZEPS sensor switch component which is deflected by the humidity-sensitive polymer comprises a silicon flexure plate with a boss structure. Such a construction offers several advantages:

- The flexure plate shows a suitable compliance with respect to a large enough deflection for the switching movement.
- The boss structure itself serves as the switching contact.
- Switching electrical contacts needs a switching hysteresis to avoid oscillations, to achieve fast switching and to apply a sufficient contact force. Such a snap behavior can be realized by applying a preload through e. g. an oxide layer onto the silicon flexure plate.

Due to the miniaturized dimensions of MEMS-based sensors only low contact forces (< 1 mN) can be generated. To minimize the necessary contact force and the contact resistance and to improve the reliability gold nanowires were used as a backplate electrode (Figure 3) [11]. The gold nanowires were manufactured by the group of Prof. H. Schlaak at EMK of TU Darmstadt using optical lithography, galvanic processes and the use of a poly(l carbonate template which is described more detailed in [12] [13].

Figure 3: SEM image of Au nanowires with high density of about 108 / cm², 200 nm diameter, 18 μm length and aspect ratio of 90:1 as part of a contact electrode [12]: a) overview, b) detail

2. EXPERIMENTALS

2.1 Manufacturing of the humidity sensitive hydrogel

One key element of the BIZEPS platform is the sensitive polymer layer which interacts with the parameter to be measured, here the relative humidity. A hydrogel blend of 15 wt% poly(vinyl alcohol) (PVA, molecular mass $M_w = 89,000 \dots 98,000$) and 7.5 wt% poly(acrylic acid) (PAA, $M_v = 450,000$) in a mass ratio of 4:1 is used. Both materials (Figure 4a,b) were purchased at Sigma-Aldrich. The powders were solved in deionized water and mixed for several hours at 80°C until homogenous solutions were formed. Then both polymer solutions were mixed to form the hydrogel blend.

Figure 4: Used polymers: a) poly(vinyl alcohol), b) poly(acrylic acid), c) (3-Amino-propyl)triethoxysilane (APTES)

2.2 Manufacturing of the hydrogel layer

In order to define the bending direction of the silicon plate due to hydrogel swelling the hydrogel layer has to be patterned in a proper way. Suitable processing technologies of the hydrogel blend are mainly restricted by the high viscosity, the volume shrinking when the solvent is evaporating and the fragile silicon plate where the hydrogel has to be coated on. Different techniques were tested and the inverse silicone stamping has been proved to be an advantageous technology (Figure 5).

Figure 5: Inverse silicone stamping to pattern the humidity-sensitive hydrogel layer (explanation in the text)

For this, silicone stamps (Figure 6a) were punched out of a Sylgard-184 layer (Dow Corning) by using biopunchers (Harris Uni-Core) of 1.5 ... 3 mm in size. The silicone elastomer kit of Sylgard-184 consists of two liquid components, the base PDMS and the crosslinking agent. Both components were mixed in a 10:1 ratio by weight. After preparing the silicone stamps a thin adhesion layer was coated in the cavity of the cleaned silicon chips using a 3% 3-Aminopropyltriethoxysilane solution ($\text{C}_9\text{H}_{23}\text{NO}_3\text{Si}$, APTES) (Carl Roth) (Figure 4c) based on acetone. The formed layer was cured and activated at 90°C for about 10 min (Figure 5a). Then the silicone stamp was positioned and brought into contact with the silicon membrane. Due to the light sticking of the PDMS a weak bond to the membrane is formed. The degassed hydrogel blend was filled with a pipette into the remaining cavity with a height of about 370 μm (Figure 5b). At this step it is crucial that no air bubbles are entrapped or remain, especially at the surface of the stamp, which would otherwise lead to an inhomogeneous layer. The evaporation of the solvent water is accelerated by a temperature of 50°C (Figure 5c). Here, the time until the stamp is removed is very important to prevent that the hydrogel adhering to the stamp does not form a wall-like structure. Depending on the viscosity of the hydrogel blend, which is mainly influenced by the water content, a layer of about 15 μm in thickness is formed (Figure 5d). Finally, the crosslinking of the hydrogel is done at a temperature of 130°C for 20 min.

Figure 6: a) Silicone stamps with a diameter of 2 mm, b) properly crosslinked hydrogel layer

2.3 Experimental set-up

The deformation of the silicon membrane was studied according to the Figure 7a with a 3D profilometer (μ Scan, NanoFocus, Germany) and a chromatic sensor. The neutral position of the silicon membrane was chosen as the reference point ($w_0 = 0 \mu\text{m}$). This corresponds to the position of an uncovered membrane in a normal environment without any hydrogel. The edge of the membrane is fixed due to the silicone frame. For the silicon chip with a boss structure, w_0 corresponds to the height $h_B = 35 \mu\text{m}$ of the boss. The so prepared chip is placed in a closed humidity chamber possessing a glass window with a high optical transparency in the range of the chromatic light. The defined moistened air (2 ... 95% r.H.) is provided through the inlet into the chamber and is monitored with a humidity-temperature sensor (HYTELOG USB, B+B SENSORS, Germany) (Figure 7b). With this measurement set-up it is possible to repeatedly scan the whole membrane. For an area of 6 mm x 6 mm and a scanning x-resolution of $2 \mu\text{m}$ and a y-resolution of $100 \mu\text{m}$, a full scan takes about 4 minutes. The z-resolution amount to approx. 10 nm. The obtained 3D-data was fitted with a median filter of 10 pixels to smoothen the data.

Figure 7: Measuring set-up: a) sample with hydrogel in the laser scanning profilometer and b) humidity chamber

Figure 8: Measuring set-up

3. RESULTS AND DISCUSSION

3.1 Deformation experiments

In order to study the deformation behavior of the hydrogel-coated membrane, a reference chip with a membrane of 5 mm x 5 mm in size without a boss structure was considered. According to Figure 7 and 9 the membrane is deformed in the direction of the hydrogel when the hydrogel is dried (at 6% r.H.). A deformation range of $-7,6 \dots -16 \mu\text{m}$ was measured. Afterwards, the air was moistened to 90% r.H. Approximately 20 min later the membranes reached their maximum deflection in the positive direction relative to the neutral position in a range of $6,6 \dots 9 \mu\text{m}$. In total a deformation of $15 \dots 24 \mu\text{m}$ has been detected. The response time of about 20 min (Figure 9b) is sufficient for the intended application as an environment humidity sensor switch. For a membrane with a boss structure this deformation behavior would result in the closing of the electrical micro contact. However it is obvious that the absolute negative deformation is bigger than the positive one. The reason for this is related to the way the hydrogel layer was coated onto the membrane. It was deposited as a blend directly on top of the membrane, was dried and then crosslinked. By this procedure the patterned hydrogel layer already causes a shear tension in the membrane. This is due to the bimorphic effect while the hydrogel layer is drying which results in a deformation into the negative direction. A remoistening will result in an opposite tension through the reswelling until the neutral position is reached again.

It is important how much water could be absorbed from the water vapor in the air. Unfortunately, as it was described already in [8], the maximum volume swelling of this PVA/PAA layer in moistened air is only approximately 20% which is much less than what can be seen in a pH buffer solution ($> 100\%$) [9]. Because the hydrogel is already swollen lightly in the neutral position there does not remain that much reserve of volume swelling. This could be one reason for the smaller deformation in the positive direction. Another reason could be the decreasing elastic modulus when the hydrogel is swelling. This behavior has an important impact on the bonding between the transducer system and the substrate with respect to the electrical micro contact. They have to be bonded to each other in such a way that the contact is already closed by the boss structure. If the hydrogel layer is coated to the membrane then the switch will be opened in dry environments and be closed in humid ones.

Figure 9: a) Deflection of membranes caused by hydrogel swelling, b) time until the maximum deflection

In the next step the reproducibility of the deformation was investigated (Figure 10). The samples were stored and dried in a desiccator for at least 24 hours. Then they were put in the measuring set-up and several moistening (90% r.H.) and dehumidification (6% r.H.) cycles were carried out. Each step was changed after 26 min. The deformation seems to be sufficiently reproducible. Also the response time is low enough ($\tau \leq 8$) while the deformation range amounts to approx. $10 \mu\text{m}$. However, it can also be seen that the initial deformation is not reached at the end of the dehumidification phase. This is an expected behavior caused by different transportation processes [10] for the swelling and deswelling phase in the hydrogel.

Figure 10: Time-dependent deformation w of a PVA/PAA hydrogel-coated silicon membrane (20 μm in thickness) due to cyclic moistening and dehumidification (6 ... 90% r.H.)

To find out if the swelling for a given constant relative humidity reaches a saturated state, the samples with a hydrogel layer thickness of about 15 μm were dried in a desiccator for at least 24 hours and then put in the measuring set-up. Then the relative humidity was increased stepwise every 90 min while the resulting deformation was monitored (Figure 11). The temperature was held constant at RT. The result shows that the higher the relative humidity was chosen the much faster a saturated state could be reached. The greatest change of deformation of about 7 μm was measured in the range of 60% r.H.

Figure 11: Time-dependent deformation w of a PVA/PAA hydrogel-coated silicon membrane (thickness 20 μm) due to stepwise moistening (6 ... 80% r.H.)

In order to study the effect of water loading of the PVA/PAA layer more in detail the water vapor sorption was measured gravimetrically (TGA-Q5000, TA Instruments). Samples with a thickness of 15 μm has been prepared and cut to small pieces of about 1.84 mg in dry state. During the measurement the temperature was held constant at 20°C while the relative humidity was increased discretely in steps of 10%. The results are shown in Figure 12. It can be seen that a small water load is already achieved with 40% r.H. but the time to reach a saturated value is still very high with up to 5 hours. In contrast to this for a relative humidity of more than 70%, the loading increases noticeable higher per step in a much shorter time frame (< 1.5 h). Here, the time constant when 63% of the saturated value is reached, is less than 20 min for humidity values higher than 70% r.H. This fact corresponds well to the results taken with the NanoFocus μScan 3D profilometer. As a consequence, a PVA/PAA layer in combination with the transducer system of the sensor switch is well suited for measuring relative humidity values of more than 70%.

Figure 12: Water load vs. time in dependence of the relative humidity of a 15 μm PVA/PAA layer at 20°C

Figure 13: Water load vs. time in dependence of the temperature of a 15 μm PVA/PAA layer at 60% r.H.

The influence of the temperature on the water load of a 15 μm PVA/PAA layer was also studied gravimetrically with the TGA-Q5000. The relative humidity was held constant at 60% (Figure 13) and the temperature was increased discretely in steps of 10%. The water uptake at the beginning of the measurement is a result of the increasing relative humidity up to 60%. From here the following changes are driven by the temperature. It is obvious that a light decreasing water load occur with increasing temperature. However, this decrease of the water load of less than 0.003 g H_2O / g TM seems to be insignificant compared to the change of the relative humidity for the intended application.

4. CONCLUSIONS

Binary zero-power sensors allow the monitoring of the relative humidity. This is achieved by using a humidity-sensitive hydrogel as transducer element. If the hydrogel swells or shrinks then the silicon flexure plate serving as switching element will be deflected. It was found that the transducer and the substrate with the electrical micro contact have to be bonded in such a way that the contact is already closed by the boss structure. After coating the hydrogel layer onto the membrane the switch will be opened in dry environments and be closed in humid ones. Reproducible deformations of up to 15 ... 24 μm for a 5 mm x 5 mm silicon membrane has been measured. Investigations of the swelling kinetics showed a saturation of the water load. The corresponding time constant is decreasing by increasing the relative humidity. A significant influence of the temperature to the water load could not be observed.

ACKNOWLEDGMENT

This work was supported through the DFG Research Training Group GRK1865.

REFERENCES

- [1] Frank, T., Gerlach, G., Steinke, A., "Binary zero-power sensors: an alternative solution for power-free energy-autonomous sensor systems", *Microsystem Technologies*, vol. 18, issue 7-8, 1225-1231 (2012).
- [2] Rittersma, Z. M., "Recent achievements in miniaturised humidity sensors – a review of transduction techniques", *Sensors and Actuators A: Physical*, vol. 96, 196-210 (2002).
- [3] Batumalay, M., Harun, S.W., "Relative humidity measurement using tapered plastic fiber coated with HEC / PVDF", 2013 International Conference on Technology, Informatics, Management, Engineering & Environment (TIME-E 2013), (2013).
- [4] WO2009077446A1 (25.06.2009), Technische Universität Ilmenau.
- [5] Chen, L.-T., Lee, C.-Y., Cheng, W.-H., "MEMS-based humidity sensor with integrated temperature compensation mechanism", *Sensors and Actuators A: Physical*, vol. 147, Elsevier, 522-528 (2008).
- [6] Miyata, T., Uragami, T., Nakamae, K., "Biomolecule-sensitive hydrogels", *Advanced Drug Delivery Reviews* 54, Elsevier, 79-98 (2002).
- [7] Reichl, D., "Aufbau, Charakterisierung und Optimierung eines optischen Sensorsystems zur reflektometrischen Interferenzspektroskopie mit mehrfarbigen Leuchtdioden", Dissertation, Eberhard-Karls-Universität Tübingen, (2000).
- [8] Bellmann, C., Sarwar, R., Steinke, A., Frank, T., Schlaak, H. F., Gerlach, G., "Development of a humidity micro switch based on humidity-sensitive polymers", 23rd Micromechanics and Microsystems Europe Workshop (MME), (2012).
- [9] Richter, A., Bund, A., Keller, M., Arndt, K.-F., "Characterization of a microgravimetric sensor based on pH sensitive hydrogels", *Sensors and Actuators B: Chemical*, vol. 99, 579-585 (2004).
- [10] Guenther, M., Gerlach, G., Sorber, J., Suchanek, G., Arndt, K.-F., Richter, A., "Chemical and pH sensors based on the swelling behavior of hydrogels", *Sensors and Actuators B: Chemical*, vol. 111-112, 555-561 (2005).
- [11] Baek, S. S., Fearing, R. S., "Reducing contact resistance using compliant nickel nanowire arrays", *IEEE Transactions on Components and Packaging Technologies*, Vol. 31, No. 4, (2008).
- [12] Quednau, S., Schlaak, H. F., "In-Situ Erzeugung von Arrays aus metallischen Mikro- und Nanodrähten in Silizium-Mikrosystemen", *Mikro-Nano-Integration (GMM-FB 68) – 3. GMM Workshop*, (2011).
- [13] Quednau, S., Dassinger, F., Schlaak, H.F., "Growth In-Place Integration of Metallic Nanowires into MEMS Gas Flow Sensors", *Sensors and Measuring Systems 2014*, (2014).