Proceedings

Fast Humidity Sensors for Harsh Environment †

Anton Buchberger [1,*], Anna Maria Coclite [2] and Alexander Bergmann [1]

[1] Institute of Electronic Sensor Systems, Graz University of Technology, 8010 Graz, Austria; alexander.bergmann@tugraz.at
[2] Institute of Solid State Physics, Graz University of Technology, 8010 Graz, Austria; anna.coclite@tugraz.at
* Correspondence: anton.buchberger@tugraz.at; Tel.: +43-316-8733348
† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 6 December 2018

Abstract: With the application of a recently developed deposition method called initiated chemical vapor deposition (iCVD), remarkably fast responsive hydrogel thin films in the order of a few hundred nanometers were created. When in contact with humid air, the hydrogel layer extends its thickness manifold, which can be detected. The verification of the thickness change was realized interferometrically with a laser and a white light input source in two different implementations. The setup was designed without electric components in the vicinity of the active sensor layer and is therefore applicable in harsh and explosive environment. The achieved response time for an abrupt change of the humidity $\tau_{63} \leq 2.5$ s is about three times lower compared to one of the fastest commercially available sensors on the market.

Keywords: humidity measurement; polymer; hydrogel; thin film; initial chemical vapor deposition; iCVD; thin film thickness; laser interference; spectral reflectance; Flory-Huggins theory

1. Introduction

Hygrometers are devices for measuring the humidity, which refers to the amount of water vapor in the air. A commonly used quantity to define this amount is the percentage relative humidity *RH*. It is defined as the ratio of the partial pressure of water vapor in the air, over the equilibrium vapor pressure of water at the given temperature [1]. Electronic measurement of humidity is the dominant technology on the market. Most of those sensors provide typical response times in the order of a few seconds. There are several fields where faster and more robust sensors are necessary, like breath recording or monitoring gas-flows [2]. The latter could contain explosive components which limits the applicability of electronic sensors further.

The presented hygrometer is a first principle measurement system, that is based on an optical measurement of the swelling of a hydrogel thin-film, which is directly related to the relative humidity of the surrounding atmosphere. In former work it was shown, that Poly 2-hydroxyethyl methacrylate (pHEMA), deposited with a method called initiated chemical vapor deposition (iCVD), provides excellent swelling behavior [3]. The correlation of the relative thickness change and the relative humidity *RH* is described by the Flory-Huggins theory which applies for the used kind of hydrogel [4,5]. The focus for the sensor development is on industrial applicability in terms of costs, dimensions and the denial of ionizing radiation.

2. Materials and Methods

The optical detection was performed with two methods, that are both based on interference phenomena. The first approach consists of a laser and a photo detector and is able to measure relative thickness changes with a time resolution of 0.1 s. The second method is implemented with a broadband light source and a spectrometer. The time resolution is lower (>3 s), but the spectral recordings yield to absolute thickness values.

The principal detection setup is sketched in Figure 1. A pure pHEMA hydrogel thin-film layer with an initial thickness of about 600 nm was deposited on a 2 mm sapphire substrate as the first prototype. In a second iteration of the setup the hydrogel got deposited onto the tip of a fiber probe. A detailed description of the deposition technique can be found in the work by Unger et al. [3]. In order to apply the sensor also in harsh environment, no parts for the optical detection were placed on the side of the hydrogel thin-film, meaning that the optical setup was installed on the backside of the substrate. The incoming field E_0 gets reflected at every interface, leading to three reflected fields that interfere with each other.

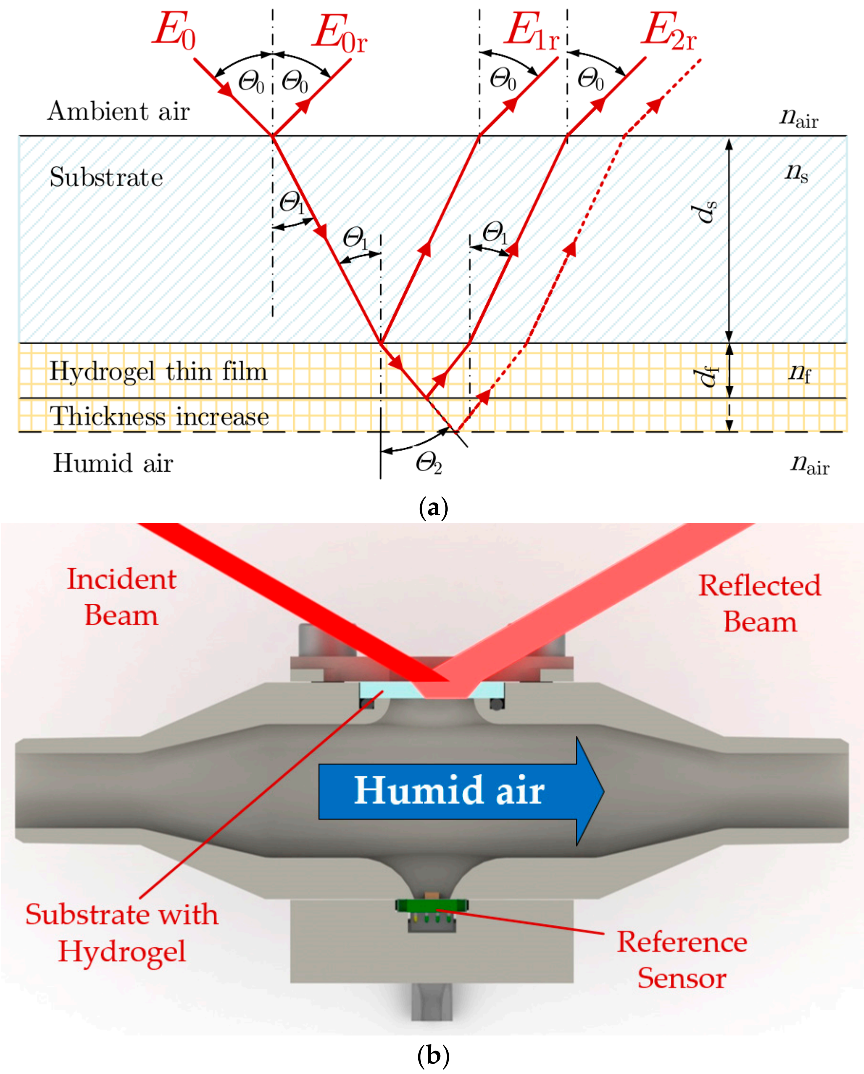

Figure 1. (**a**) Principal sketch of a field that gets reflected at a swelling hydrogel thin-film layer deposited on a substrate (thickness of the hydrogel is drawn exaggerated) and (**b**) sectional view of the practical implementation of the substrate with the hydrogel (drawn in light blue) on the measurement chamber. Reference sensor (in green) on the opposite side.

The experimental setup was implemented with the substrate mounted on the sidewall of a measurement chamber and is shown in Figure 1b. A Sensirion SHT31 (Sensirion AG, Stäfa, Switzerland) humidity sensor was installed as a reference on the opposite wall. The atmosphere inside the chamber was controlled by a direct evaporator aSTEAM DV-4 series (aDROP Feuchtemeßtechnik GmbH, Fürth, Germany), that was attached with a hose. The temperature was held constant. For the laser interference setup a Thorlabs CPS635 laser diode and a Thorlabs S120C (Thorlabs Inc., Newton, NJ, USA) photo diode was used. The spectral reflectance measurement was implemented with an Ocean Optics HL-2000-HP-FHSA tungsten halogen light source and an Ocean Optics Flame (Ocean Optics Inc., Winter Parks, FL, USA) UV-VIS spectrometer. The data for both measurement methods was recorded simultaneously. In parallel the installed humidity sensor captured a reference *RH* value. A variation of *RH* in the chamber led to a change of the thin-film thickness.

3. Results and Discussion

3.1. Thickness Measurement

Figure 2b shows a measured reflectance spectrum for one certain *RH* setting and thin-film thickness respectively. By fitting the data with the theoretic model an absolute thickness was derived. This was performed for several humidities between 3% to 97% RH. In Figure 2a the reflected laser intensity is plotted over the derived absolute thickness values. The fit with the theoretic model is in good alignment with the measured data. At film thicknesses >1000 nm the data starts to deviate from the model function. This is caused by a variation of the refractive index of the thin-film at high humidity levels, that are not taken into account by the used model.

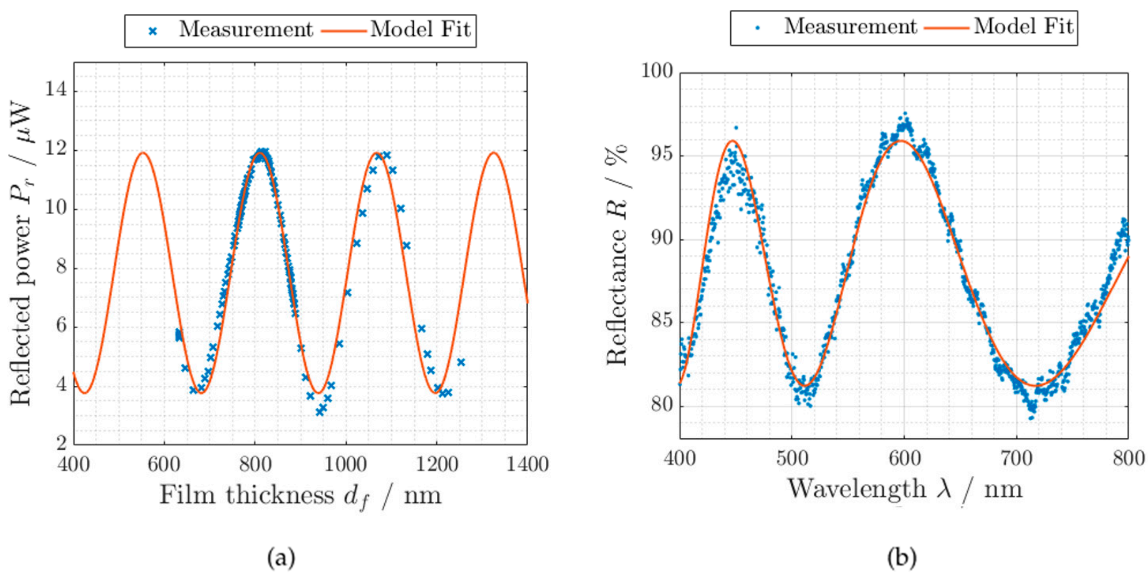

Figure 2. Measurements with corresponding model fit for (**a**) the laser interference setup for a wavelength of 635 nm at an incident angle of 60.5°, which shows the reflected power over the thin-film thickness derived by spectral reflectance measurements like the one shown in (**b**) for a certain thickness value at an incident angle of 37°.

3.2. Humidity Measurement

The correlation between the thin-film thickness and the relative humidity *RH* is described by the Flory-Huggins theory with Equation (1) [3].

$$RH = \left(1 - \frac{d_0}{d}\right) \exp\left(\frac{d_0}{d} + \chi \left(\frac{d_0}{d}\right)^2\right) \quad (1)$$

It contains just the thickness ratio d_0/d and does not require a measurement of an absolute value. As long as the total thickness increase is limited in between a maximum and a minimum of the interference curve shown in Figure 2a the laser interference measurement would be sufficient. In terms of costs, this is the preferable configuration. In the actual measurement the total thickness increase was much higher than half a period and the association between the measured intensity and the thickness was ambiguous. Therefore, the values from the spectral reflectance measurements were taken for the following evaluation. Equation (1) contains the so called Flory-Huggins interaction parameter χ, which is non-constant and specific for the used material composition (pHEMA and water). Due to lack of information in literature, calibration measurements were performed to fit this parameter with a polynomial expansion. By applying the derived χ in Equation (1) the corresponding *RH* can be calculated for every thickness value. A plot of the function is shown in Figure 3a together with measured data used for the calibration.

The evaluation of the sensor response time is plotted in Figure 3b,c. The data for the analysis was taken from the laser interference measurement, due to the higher time resolution. Hence, the top value of the applied *RH* step was limited because of the ambiguity explained before. The response time is commonly defined as the 1/e time constant τ_{63}, at which the sensor readings change 63% of the full *RH* step. The measured response times are τ_{63} = (1.5 ± 0.5) s for an abrupt signal rise and τ_{63} = (2.5 ± 0.5) s for a signal drop, which is about three times faster than the reference sensor.

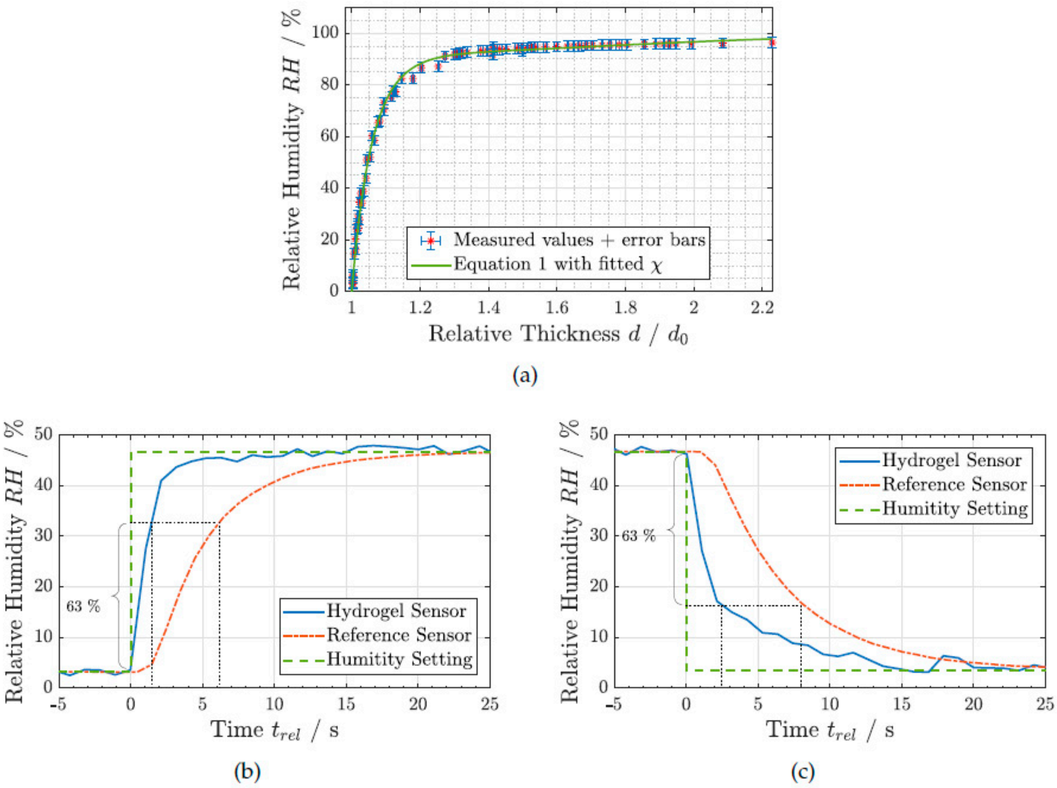

Figure 3. (**a**) *RH* calculated with Equation (1) as a function of the thickness ratio d/d_0 in comparison with measured data points and response signals of the hydrogel sensor compared to a commercial reference sensor after an abrupt change of the humidity setting for: (**b**) a humidity rise and (**c**) a humidity drop. The dotted lines indicate the response time parameter τ_{63}.

4. Conclusions

The setup reacts fast and reproducibly to changes of the humidity level. The measured response times are about three times faster compared to one of the fastest commercially available sensors. The spectral reflectance measurements covered a humidity range from 3% to 97% RH. The application range of the laser interference setup was limited to <50% RH for the used implementation. Modifications in the composition of the hydrogel and the used laser are planned for increasing the range. In a second iteration the setup was realized with the hydrogel deposited on the tip of a fiber probe, which led to similar results. Due to the lack of electric components in the sensor head, measurements in explosive environment are possible, which are matter of future investigations.

Author Contributions: A.B. (Anton Buchberger) was responsible for the conceptualization, methodology, implementation and writing; A.M.C. and A.B. (Alexander Bergmann) supervised and reviewed the project; A.B. (Alexander Bergmann) acquired the funding.

Funding: This research was funded by Austrian Research Promotion Agency (FFG) grant number 861163.

Conflicts of Interest: The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References

1. Perry, R.H.; Green, D.W.; Maloney, J.O. *Chemical Engineers' Handbook*, 7th ed.; McGraw-Hill: New York, NY, USA, 1997; p. 2433.
2. Kolpakov, S.A.; Gordon, N.T.; Mou, C.; Zhou, K. Toward a new generation of photonic humidity sensors. *Sensors* **2014**, *14*, 3986–4013, doi:10.3390/s140303986.
3. Unger, K.; Resel, R.; Coclite, A.M. Dynamic Studies on the Response to Humidity of Poly(2-hydroxyethylmethacrylate) Hydrogels Produced by Initiated Chemical Vapor Deposition. *Macromol. Chem. Phys.* **2016**, *217*, 2372–2379, doi:10.1002/macp.201600271.
4. Rubinstein, M.; Colby, R.H. *Polymer Physics*; Oxford University Press: Oxford, UK, 2003; p. 454.
5. Teraoka, I. *Polymer Solutions*; John Wiley & Sons: New York, NY, USA, 2002; p. 360.