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Untersuchung der optischen Eigenschaften von Palladiumdünnschichten in Wasserstoff für einen Chip-basierten MOEMS-Wasserstoff-Sensor

Characterizing Optical properties of Palladium thin films in Hydrogen for chip-based MOEMS hydrogen sensor

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Kurzfassung

Um den Bedarf an Wasserstoff-Sensorik für sauerstofffreie Atmosphären (Elektrolyseure, Gasverteilnetz) zu decken, wird ein innovativer Chip-basierter MOEMS-Wasserstoff-Sensor entwickelt, welcher die Änderung der optischen Transmission von Palladium unter variierenden Wasserstoff-Konzentrationen ausnutzt. Als Basis für den Einsatz der Dünnschichten in der sensorischen Anwendung wurden die optischen Eigenschaften von Palladium bestimmt und werden in diesem Beitrag diskutiert. Weiterführend sollen diese Erkenntnisse in den Kontext der Anwendung gesetzt und erste Annahmen zu Eigenschaften des Sensors getroffen werden.

Abstract

To overcome the shortage of hydrogen sensors for oxygen-free environments (electrolyzers, pipelines, etc.), we develop an innovative chip-based MOEMS hydrogen sensor using the change in the optical transmission of palladium at varying hydrogen concentrations. As a first milestone, the optical properties of palladium thin films have been characterized and will be discussed in this paper. Further, the findings are set in context to the sensor system for first assumptions on the expected sensor performance.

1 Introduction

The Palladium-Hydrogen system is a thoroughly studied system with distinctive modifications, that reveals reversible volumetric, electrical and optical changes for varying hydrogen concentrations [1]-[3]. These phenomena propagate the use for sensor systems to measure hydrogen fractions in gas mixtures. Among others, the first concept to exploit the changes in optical transmission was given by [4]. In the scope of optical sensors, a vast variety of systems were developed. Those systems are using changes in transmission or other optical phenomena and the structure of the palladium-based active layer in different compositions, with or without optical fibers [5][6].
In our setup, a palladium layer on a photodiode is used as a switchable mirror. The photocurrent correlates to the irradiation intensity, that is determined by the palladium layer and varies upon hydrogen interaction as a result. The irradiation source is a bare-die LED placed and bonded on top of the final chip with a radiant power of 6.5 mW. To compensate for varying irradiation intensity, a second photodiode is intended as a reference, a third photodiode is blocked with an aluminum layer for offset correction, and a fourth photodiode is used optionally for an additional measurement layer or layer stack. This setup could be referred to as a four-quadrant photodiode with a hybrid-packaged light source (see Fig. 1). In contrast to previous developments, our system aims to be a wafer-based, scalable and low-cost option suitable for oxygen-free environments with the potential to measure arbitrary hydrogen concentrations also above the LEL [7].

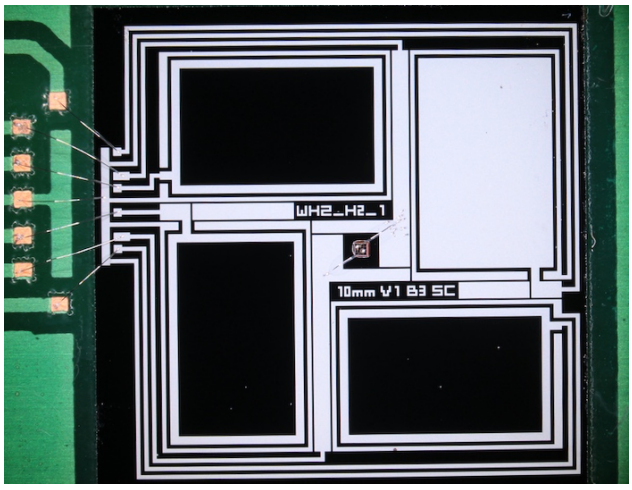

Fig. 1 Final sensor chip with four photodiodes and LED, mounted and bonded, chip size is approx. 12.6 x 12.6 mm^2

This paper reports on the basic examination of the transmission of palladium for various layer thicknesses and hydrogen concentrations. Notable observations along those measurements, concerning the formation of cracks in the film and basic dynamic properties, will be mentioned in brief. For the sensor design, the goal of this paper is to compare these findings to the spectral sensitivity of the silicon-based photodiode to derive a suitable wavelength for the

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LED on the MOEMS-chip that promises the maximum responsivity for the complete system.

2 Experimental Procedure

To assess their optical transmission, the palladium layers were deposited on samples of float glass and fused silica (18 x 18 x 0.5 mm^3) by RF-Sputtering (Bias 1000 V / 0,25 Pa / 25 sccm Ar) from a 3-inch palladium-target (99.95 % w/w, FHR Anlagenbau GmbH, Ottendorf-Okrilla). The thickness of the film was determined by extrapolating the sputter time scaled according to thicker samples measured by a surface profilometer (Dektak 150, Veeco).
The coated samples were placed inside a custom build, sealed aluminum chamber (approx. 150 cm^3) with two float glass windows (Edmund Optics BV, Best, The Netherlands). To enable the evaluation of changes in transmission, the chamber can be evacuated and flooded from a gas bag reservoir under atmospheric pressure or constantly purged with a gas mixture at varying flowrates. The gas mixture is provided by a custom build setup, where two MFCs are controlled analogously to mix nitrogen and premixed Argon-Hydrogen gas (0.95 / 0.05). A correction for the nitrogen-calibrated MFCs was applied.
This setup is placed inside a Spectrophotometer JASCO V-770 (JASCO Deutschland GmbH, Pfungstadt) to measure the transmittivity in a dual beam configuration, meaning a reference beam is tracked during the measurement to compensate for changes in the light source or the detector [8]. A correction for the transmission of the substrate in the chamber is calculated afterwards to account for losses regarding the chamber windows and the substrate and a smoothing is applied for readability. However, the fraction of light that is reflected on the first surface (from air to substrate) is not considered for being absent in the case of coated substrates. This results in a systematic error. A random error occurs from the manual installation of the setup because of geometric offsets.

3 Results

Fig. 2 shows the transmission of the Pd layers vs the wavelength in nm for thicknesses of 15 nm to 60 nm in nitrogen and in a mixture of argon and hydrogen (0.95 / 0.05). The same measurements are displayed in Fig. 3 as relative change in transmission (ratio of transmission with 5 % v/v hydrogen to without hydrogen). Transmission decreases exponentially with increasing thickness following Lambert-Beer law. The relative change in transmission increases for increasing palladium height.
It should be pointed out, that layers higher than 30 nm result in macroscopic cracks at the first exposure to hydrogen (5 % v/v in Argon), significantly affecting the repeatability. For these layers, the measurements also show a decreased signal-to-noise ratio according to the lower transmission.

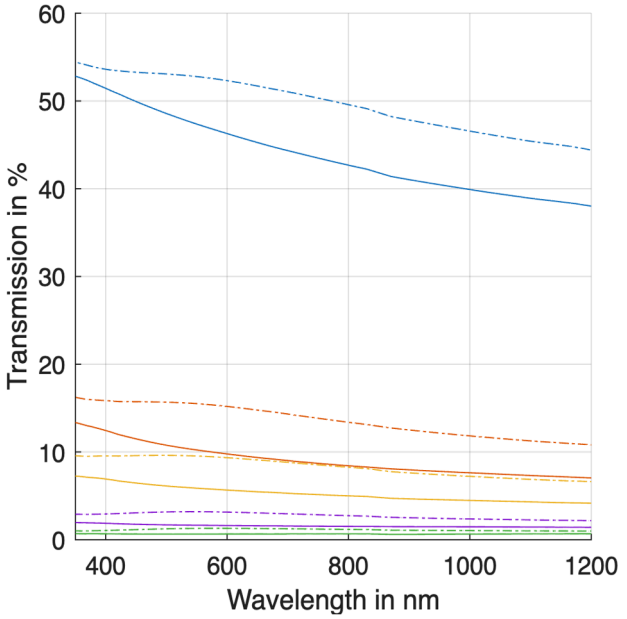

Fig. 2 Transmission of Palladium on Float Glass at 0 % (solid line) and 5 % v/v hydrogen in Ar (dash-dotted line) over the wavelength in nm for various thicknesses of Pd: 15 nm (blue), 22 nm (orange), 30 nm (yellow), 45 nm (purple), 60 nm (green).

For the relative change in transmission of layers thicker than 15 nm, a peak can be found below 800 nm. As the thickness increases, this peak develops more and shifts towards shorter wavelengths.

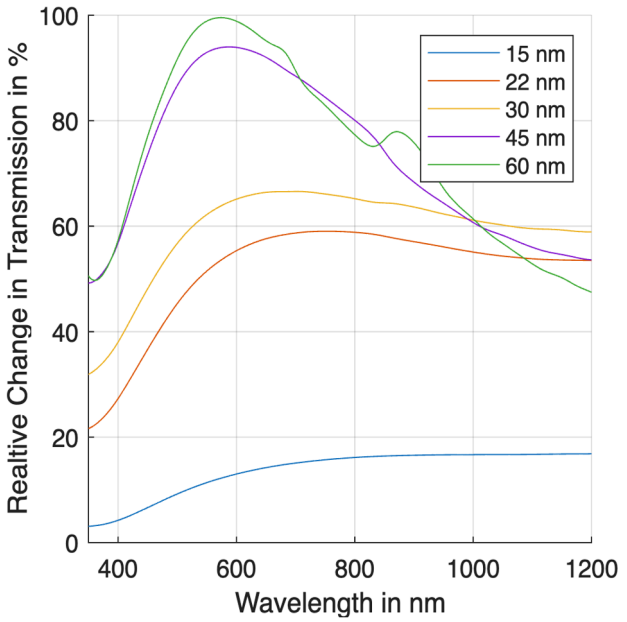

Fig. 3 Relative Change in transmission of Palladium on Float Glass for various thicknesses at 5 % v/v hydrogen in Ar compared to 0% v/v hydrogen over the wavelength in nm

To select an optimal wavelength for the 15 nm palladium layer, the spectral sensitivity of a typical silicon photodiode is plotted in comparison in Fig. 4. Regarding a limited selection of available LEDs, a wavelength of 850 nm was selected for a top-contact bare-die LED (Chips 4 Light

GmbH, Sinzing). For comparison, the absolute transmission of the 15 nm palladium layer is plotted against varying hydrogen concentrations from 0 to 5 % v/v in Fig. 5. For this layer, the relative change in transmission is more than 10 % compared to a hydrogen absent atmosphere.

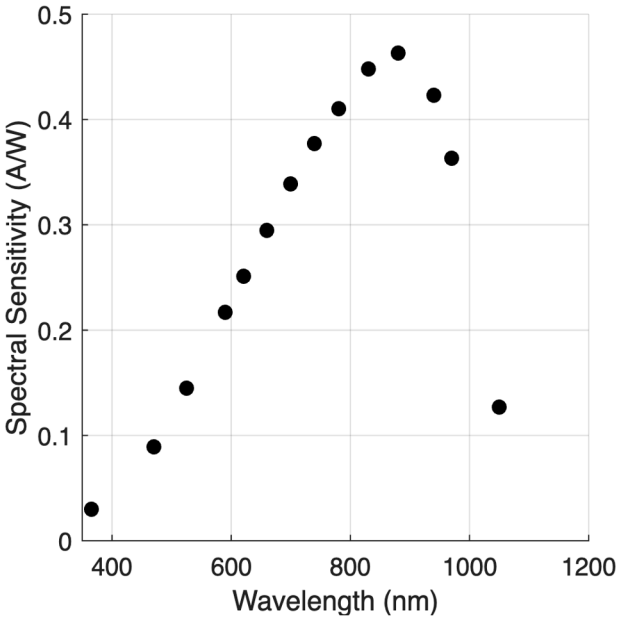

Fig. 4 Spectral Sensitivity in A/W over the wavelength in nm for a silicon photodiode (area 20 x 20 mm^2) as manufactured, referencing by measurements against calibrated equipment

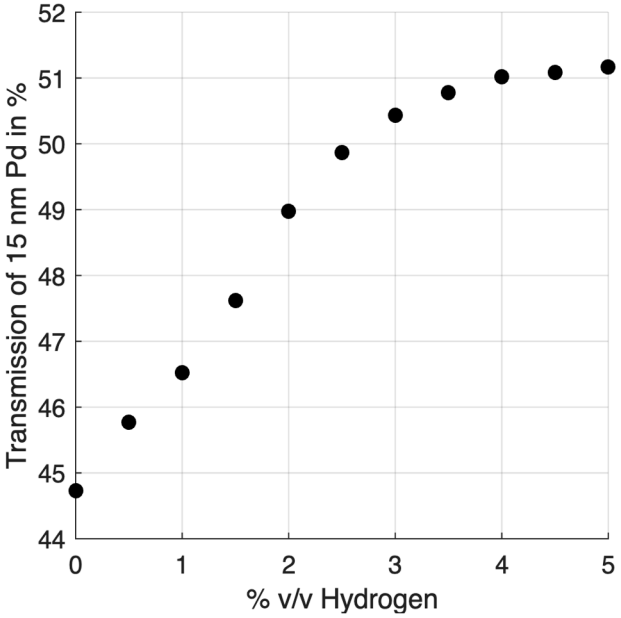

Fig. 5 Optical transmission at 850 nm of a 15 nm Pd layer on Float Glass against varying hydrogen concentrations, measured while purging at 1 slm.

During these examinations, some samples were stored in the same hydrogen containing atmosphere for 12 h. For that conditioning, also the 15 nm films show macroscopic cracks. However, these defects did not affect the change in transmission significantly. At a hydrogen concentration of 5 %, the deviation in the relative change were in range of +/- 3 % for the conditioned samples compared to the samples as manufactured. However, we noticed a change in the response time of the transmission (see Fig. 6), which will be discussed in the following.

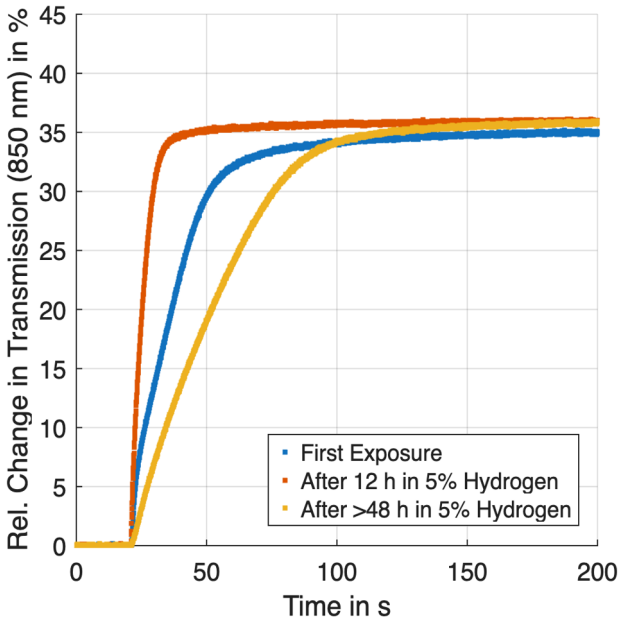

Fig. 6 Relative Change in transmission at 850 nm at a 5 % v/v hydrogen concentration compared to the transmission at 0 % v/v hydrogen transmission over time. The chamber was evacuated and afterwards flooded at 20 s with the gas mixture to atmospheric pressure.

4 Discussion

A change in transmission over the concentration of hydrogen (more precise: its partial pressure) as depicted in Fig. 5 can be related to a change in parameters of the microlattice of Pd [1]. These modifications contribute to the optical and mechanical phenomena observed in the assessed concentration range. The change in transmission flattens for concentrations higher than 3.5 %. This matches previous findings, although some change should be detectable up to 100 % with pure Pd [9]. If these changes are not sufficient for the use in the actual measurement setup, an active layer either with material compositions or layers of other materials with a Pd capping layer can be used as implemented in [10].

Regarding the mechanical stability and crack formation of the films, the effects on the sensor performance should be questioned. If a continuous exposition to hydrogen atmospheres does not affect the sensor performance, further steps may be oblique. This needs to be tested in following studies, e.g. at various concentrations and temperatures. To compensate these flaws, an adhesion layer of titanium underneath the Pd layer could be used, although its thickness should be optimized in respect to the optical transmittance. Another option might be the application of a nanostructure, which can not only improve adhesion, but could also enhance the dynamic properties of the film's transmission change.

Up to now, no evaluation of rise and fall times were successful and reproducible despite different measurement settings (flooding or purging) probably due to thermal effects during irradiation. Following established procedures, the transmission was measured against time for varying mixtures of gas while purging the chamber. Since a systematic error occurs from the time to establish the intended concentration inside the chamber, another method was used. Instead, the chamber was evacuated first with a diaphragm pump and then flooded with a gas mixture from a gas bag reservoir at atmospheric pressure as stated above. Even for this procedure, no correlation was found between the varying response times of the transmission change and other parameters. Recent additional measurements point towards the influence of the Pd film's temperature, since the irradiation of the samples took place during the evacuation. different substrate temperatures could be a consequence. If this is true, it could lead to the different response times and could explain the missing correlation [11]. This needs to be validated by additional measurements with a constant irradiation time.

The use of nanostructures in the sensor design could offer advantages in the film stability, higher absolute transmission and response times < 5 s as preliminary tests showed. To compensate for lower transmission when using multiple layers, the decrease in reflectivity by sub-wavelength structures can be of interest. One promising approach is the inhouse full wafer pattering via Displacement Talbot Lithography that is currently researched [12].

5 Conclusion and Outlook towards sensor performance

The acquired transmission data supports the intended working principle of the sensor in oxygen-free environments in the range of up to 5 % v/v hydrogen. A non-linear response can be assumed as expected. The mechanical stability of the palladium layers should be evaluated for the sensor system regarding a required preliminary conditioning of the films.

Besides the mentioned considerations about the layer, the electronic sensor system will be completed in the distant future. This includes, inter alia, the design and manufacturing of a PCB based on an ATmeag328P with an appropriate Transimpedance-Amplifier of suitable gain, an ADC device as well as an I^2C-Interface.

For the final system, the response time will be evaluated at higher hydrogen concentrations and/or with different background gases (possibly including CO, CO_2, H_2S, CH_4, H_2O vapor, among others). Finally, a temperature-dependent calibration is required and an option to measure the temperature on the sensor by resistivity or forward bias shift should be considered.

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7 Literature

[1] Manchester, F. D et al.: The H-Pd (Hydrogen-Palladium) System. Journal of Phase Equilibria 15 (1), 1994, p. 62–83.

[2] Hübert, T. et al.: Hydrogen Sensors – A Review. Sensors and Actuators B: Chemical 157 (2), 2011, p. 329–52.

[3] Palm, K. J. et al.: Dynamic Optical Properties of Metal Hydrides. ACS Photonics 5 (11), 2018, p. 4677–86.

[4] Butler, M. A.: Micromirror Optical-Fiber Hydrogen Sensor. Sensors and Actuators B: Chemical 22 (2), 1994, p. 155–63.

[5] Darmadi, I. et al.: Bulk-Processed Plasmonic Plastic Nanocomposite Materials for Optical Hydrogen Detection. Accounts of Chemical Research 56 (13), 2023, p. 1850–61.

[6] Bramann, G. et al.: New Optical Hydrogen Sensor with Fast Response Time Based on Multilayer Palladium-Nickel-PTFE Thin Film for Explosion-Proof Detection of High H2 Concentrations of 1-100%. Third European Workshop on Optical Fibre Sensors, Juli 4th, 2007, 66191L.

[7] Schröder, V. et al.: Sicherheitstechnische Eigenschaften von Erdgas-Wasserstoff-Gemischen. Abschlussbericht zum Forschungsvorhaben 2539, Bundesanstalt für Materialforschung und –prüfung (BAM). Berlin, 2016.

[8] https://jascoinc.com/products/spectroscopy/uv-visible-nir-spectrophotometers/models/v-770-uv-visible-nir-spectrophotometer/. Accessed on: 24.11.2025.

[9] Mandelis, A. and Garcia, J. A.: Pd/PVDF Thin Film Hydrogen Sensor Based on Laser-Amplitude-Modulated Optical-Transmittance: Dependence on H2 Concentration and Device Physics. Sensors and Actuators B: Chemical 49 (3), 1998, p. 258–67.

[10] Bannenberg, L. et al.: Tantalum-Palladium: Hysteresis-Free Optical Hydrogen Sensor Over 7 Orders of Magnitude in Pressure with Sub-Second Response. Advanced Functional Materials 31 (16), 2021, p. 2010483.

[11] Shutaev, V. A. et al.: Kinetics of Changing in Optical Transmittance of Palladium Nanolayers during Interaction with Hydrogen. Optics and Spectroscopy 131 (3), 2023, p. 178–82.

[12] Solak, H. H. et al.: Displacement Talbot lithography: a new method for high-resolution patterning of large areas. Opt. Express 19, 2011, p. 10686-10691.