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Optimization of Hydrogen Alarm Sensor on Semiconductor Basis

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Abstract A semiconductor based hydrogen sensor system was optimized by various modifications, which allow an improved detection of very low concentrations of hydrogen in air. The foundation for new investigations on the sensor structure are modifications of substrate and gate structures. Establishment of reference structures is a major aim. A possible drift compensation could be the use of aluminum or alloys for sensor system in order to stabilize signal in Metal Oxide Semiconductor (MOS) respectively Metal Electrolyte Insulator Semiconductor (MEIS) structures. Gold is more likely not capable to function for drift compensation as a pure metal. Nafion^{TM} treatment for cover up the palladium gate seems not to be suitable as a reference, besides could be an option to stabilize sensor signal responses and protect sensors from environmental influences.

Introduction

Hydrogen is one of the most important molecules for the future. It will have a key role for energy storage, transportation and also for processing in order to decarbonize energy demanding industry. Whereas it has an enormous potential to drive the decarbonization the future economy, it is also an explosive gas, which has to be handled with care. To make the whole hydrogen infrastructure viable and reduce risks reliable sensor systems are necessary. There are different sensor mechanisms for detecting hydrogen in air in order to form a reliable alarm scenario. All types have advantages and disadvantages concerning to their application field for Pd based Devices [1]. A good compromise of sensitivity, reliability and great mass market potential are semiconductor based sensor devices[2]. They are already widely spread on the market, because they are easy to produce in large amounts for a good price [3]. Still some negative effects like signal drift, hysteresis, energy consumption and crosstalk are tried to be reduced. One approach to minimize some potentially negative aspect was the establishment of a solid electrolyte layer on top of the insulator of a MOS (Metal Oxide Semiconductor) device to form a MEIS (Metal Electrolyte Insulator Semiconductor) structure [4]. The additional applied LaF_3 layer grants high physical stability and a broad measurement range which enables a high concentration range for hydrogen detection in air. Another positive aspect is the low energy demand of the system[5], which enables a possible use in decentralized applications also in combination with alternative energy supplies.

The solid basis of this sensor is going to be improved by the establishment of different mechanisms. Setup of various reference structures to compensate negative sensor behavior is investigated. First of all reference structures made of different metals are tested and also polymer coatings. As model systems here gold and aluminum are investigated for reference metal gates on sensors. Nafion^{TM} membranes were used for selective coating on the gate and tested for the response on hydrogen. Nafion^{TM} 117 was investigated also for Proton Exchange Membrane (PEM) water electrolysis [6] and showed positive effects for stabilizing processes at high pressure.

Setup

For the establishment of sensors 4 inch silicon wafer based material covered with an isolater layer consisting of SiO_2 and Si_3N_4 is prepared. For special features LaF_3 layer is added on top by thermal evaporation. The sensitive gate material is deposited with sputtering as a top layer on the solid electrolyte (Fig. 1). Different materials (Pd, Al, Au) and Nafion^{TM} polymer structures are tested for hydrogen response.

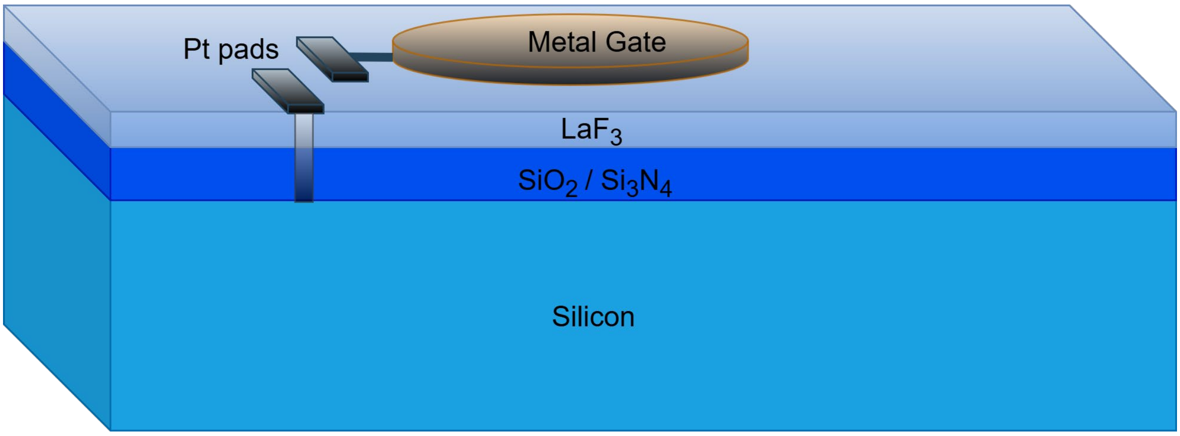

Fig. 1. Lateral cut of sensor with layer structure

As the functional gate the metals are deposited at 1Pa in an Ar Plasma. All gates have a circle shape, a diameter of 2.5 mm and a thickness of 20 nm. Nafion^{TM} 117 was used as a 5% liquid solution in lower aliphatic alcohols and water from Sigma. Different Nafion^{TM} layers were established and responses to hydrogen were measured. An amount of 3 µl was disposed by pipette to create a layer which covered the whole sensitive gate area (in that case palladium). After each layer was deposited the polymer was dried at room temperature and heated up with 100°C air stream for 5 seconds. The sensors were tested with 0 Nafion^{TM} layer, 1 Nafion^{TM} layer and 4 Nafion^{TM} layers. Shortly after deposition Layers were dried under laminar air flow, heated for 10 seconds at 100 °C and measured. The layers were also measured after defined (1 day, 2 days, 1 week, 3 weeks, 1 month, etc.) time periods to record long term behavior.
For all experiments to characterize the sensors gate signal shift of capacitance from gate to bulk a special setup was used (Fig. 2). Two different gas container (one standard artificial air 5.0 and one hydrogen 5.0) were used. To arrange a certain hydrogen concentration mass flow controllers (MFC) were established and due to different flow rates specific concentrations could be granted in the measurement cell. Measuring conditions were 24°C / 26°C, flow 1l/min in dry gas.

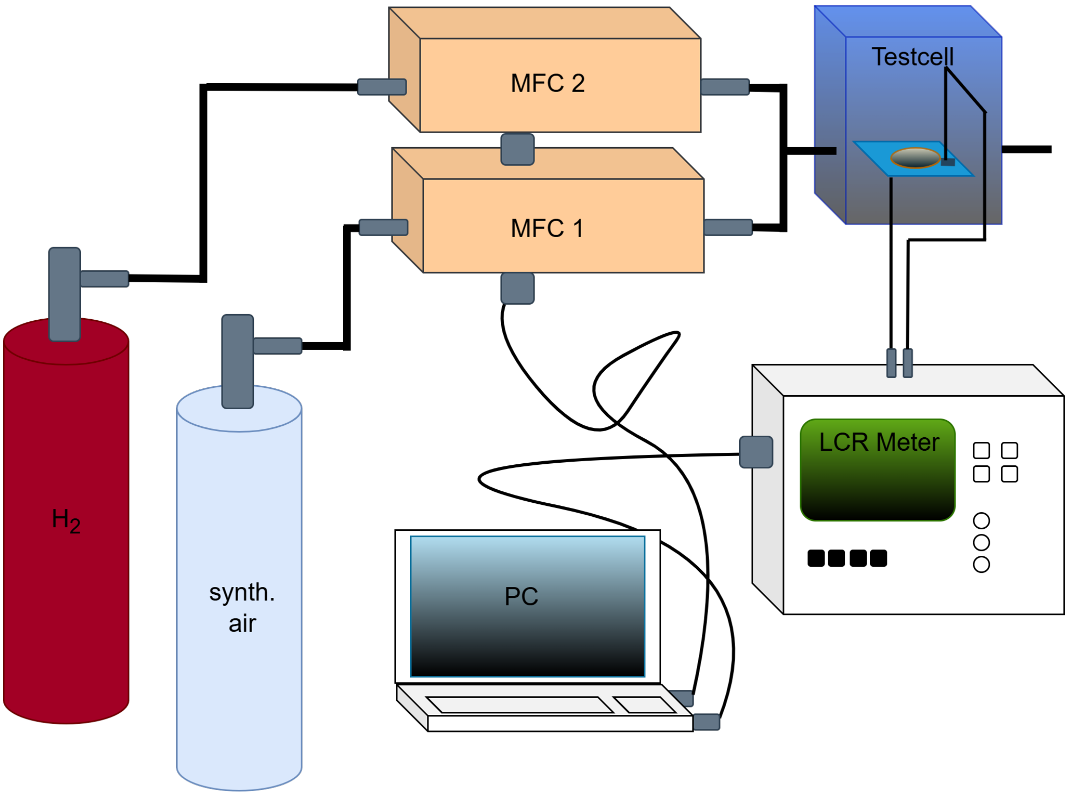

Fig. 2. Experimental measurement setup for sensor charcterization

The MFCs were controlled by a computer and the measurement of the capacitance/voltage at a frequency of 10 kHz was realized by a LCR meter (electronic measurement device to measure inductance [L], capacitance [C] and resistance [R]). A labview program was used to to synchronize the signals to the flow and log the experimental data. Two different hydrogen concentrations were set up in general. The measuring cell was loaded with 3000 and 8000 ppm H_2 in artificial air for first responses and the results were documented.

The standard measuring profile includes a base flow of 1l/min of artificial air. In general base air flow of dry synthetic air 5.0 was set up from 0- 450 seconds. Afterwards from 450 seconds hydrogen with a concentration of 3000 ppm was applied until 900 seconds of process time. The following period sensors were flooded with artificial dry air at 1l/min in order to enhance desorption of hydrogen from the gate and improve performance for next hydrogen concentration measurement. From 1400 to 1530 seconds the hydrogen concentration was set up to 8000 ppm (respectively 0.8 %) which is the lower pre alarm limit for hydrogen sensors. Due to production characteristics and semiconductor specifications sensors differ in their base parameters. For evaluation of sensors and better comparability between sensors of different charges signals were normalized. For investigations of the effect of Nafion™ coatings measurements in different time periods were made and long time behavior documented.

Results

Measured sensors with different metal gates only showed hydrogen sensitivity for palladium. Aluminum and gold just show a signal drift behavior (Fig. 3).

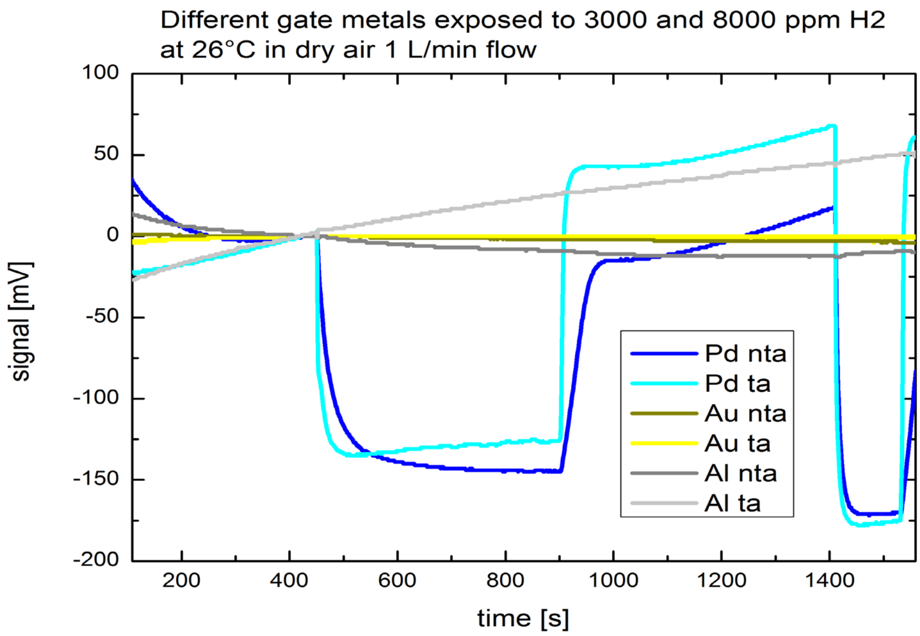

Fig. 3. Exposure of various gate metals to 3000 and 8000 ppm H2 in dry air at 1l/min (nta: not thermically activated, ta: thermically activated)

Obviously palladium coated sensors which are thermically treated show better performance when it comes to sensitivity. Faster response and higher voltage signals are plain evidence. Aluminum which was thermically activated shows a positive drift behavior, which is comparable with the palladium gate drift behavior, while gold gates and not activated aluminum gates showed negative tendency. Investigations with Nafion™ distributions showed a time dependent behavior (Fig. 4).

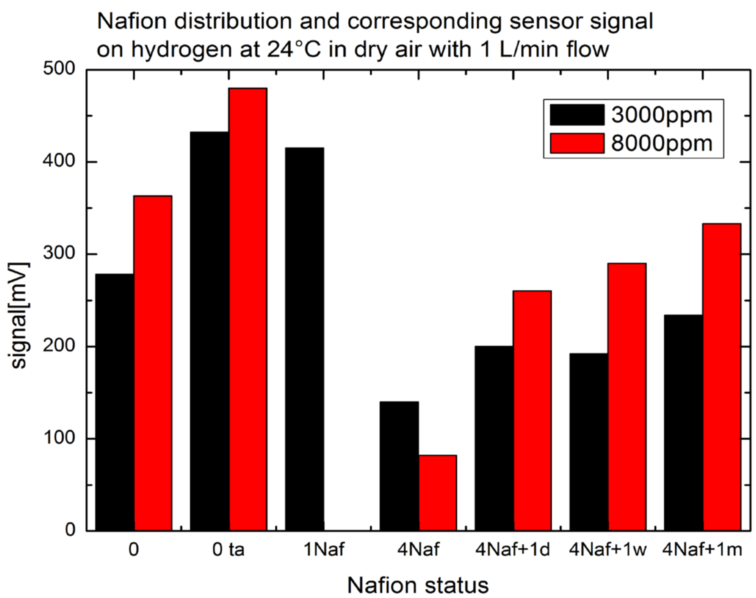

Fig.4. Nafion™ treatment and sensor response on 3000 and 8000 ppm H_2 in dry air at 24°C and a flow of 1l/min

Palladium coated sensors without Nafion™(0) were measured as a base signal. Afterwards those sensors were thermically treated (0 ta) to enhance performance. For plain palladium layers the signals both for 3000 and also for 8000ppm hydrogen were much higher. The first deposited layers of Nafion™ on palladium (1Naf) showed a comparable response on 3000 ppm of hydrogen to sensors without Nafion™. Only for 8000ppm hydrogen the measurements showed negative net

signals. With 3 additional Nafion coatings (4Naf) the measurement immediately after application showed Voltage signals which were about 50% of initial values. Measurements after one day (4Naf+1d), one week (4Naf+1w) and one month (4Naf+1m) showed a time dependent behavior of the hydrogen concentration to voltage signal.
For all Nafion™ coated sensors reduced signals could be detected. Special behavior can be observed right after depositing the 1st Nafion™ coating. Results of all investigated sensors of different charges show similar behavior (Fig. 4).

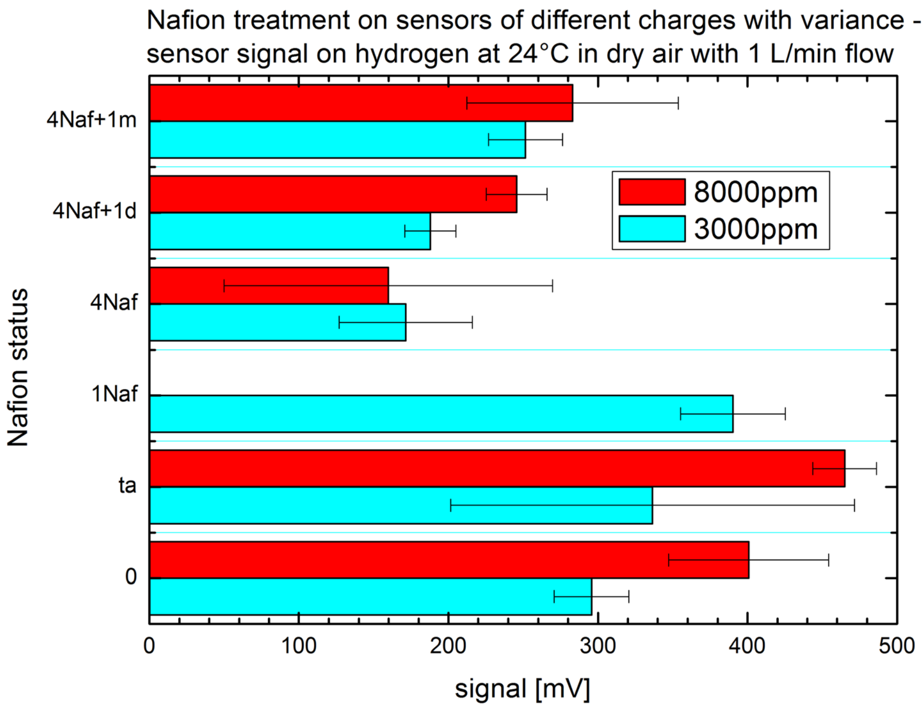

Fig. 5. Nafion™ distribution on sensors of different charges/mean sensor response on 3000 and 8000 ppm H_2 in dry air at 24°C, flow of 1l/min, with standard deviation

Thermal treatment generally showed improved hydrogen signal response (higher sensitivity and faster response time) on sensors for plain Pd and additional Nafion™ coated sensors. One layer of Nafion™ directly after depositing showed negative voltage signals for all sensors at 8000ppm hydrogen measurement. Measurement after one day showed signals of 190 mV for 3000ppm and 250 mV for 8000ppm. Higher standard deviations were documented for fresh prepared Nafion™ coatings (1Naf and 4Naf). Aging of sensors with Nafion™ coatings had showed an effect of higher net signals for all sensors. Standard deviations were lower for shorter time periods (4Naf+1d) and increased for long time observation (4Naf+1m).

Discussion and Forecast

Results show that for investigated metals Al and Au no significant hydrogen signal can be detected. Since documented drift behavior of Au is different from Pd, it is rather not valid for a potential drift compensation. In fact, especially after thermal treatment aluminum could be an option for a compensation structure, because the signal drift appears comparable.
For alarm sensors thermically treated sensors have an enhanced performance in sensitivity and a much lower response time. In contrast it is consuming energy to heat up sensors. So for battery powered sensors there should be found a compromise to meet demands of application and necessary establishment of heating programs.

Nafion™ treatment results showed unstable sensor behavior for time right after depositing the polymer layer. Aged polymer layers rather showed effects of stabilized sensor signals. Especially experiments directly after treatment showed negative signals for 2nd hydrogen concentration of 8000ppm hydrogen measured. This effect could be based on trapping hydrogen in the uncured polymer layer and decreases desorption process, while the next hydrogen measurement showed not the full sensor response as voltage signal. Additional time reduced the effect and sensors showed more characteristic Pd sensor behavior, besides signals were lower with polymeric layers.
In further investigations further metals and also alloys with palladium are going to be tested and the aluminum test series are going to be intesified. Nafion™ could play a role on further investigations, when it comes to protective covarage and stabilizing sensors, whereas it causes loss of sensitivity. Also storage conditions of polymer coated sensors and methods of thermal reactivation are of interest and should be investigated in upcoming research. Eventually other polymers can be considered as stabilizing or protective coatings, as well.
Moreover it is planned to create models and build up some simulations which are validated on experimental data. This should enable a certain forecast on alloy mechanisms for the sensor system.

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