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Sensor high throughput screening using photocurrent measurements in silicon

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Abstract

A new high throughput screening method to characterise alloys used as gate metal of Metal/solid Electrolyte/Insulator/Semiconductor (MEIS) gas-sensors was developed. Samples with continuous gradients in alloy concentration for the system $Pd_{1-x-y}Ni_yCo_y$ were analysed regarding H_2 sensitivity. First results showed reduced poisoning effects of H_2S for Ni concentrations between 4-11 at-% in Pd.

Keywords: LAPS; ternary alloy; MEIS sensor; H_2 sensor, high throughput screening

1. Introduction

Hydrogen is promising for prospective matters of energy storage and has gained more and more attention over the recent years. Since H_2 is not detectable for by human senses at all, sensors are required to avoid the risk of fire or devastating explosions e.g. the explosion of the Fukushima/Japan power plant in 2011. In literature many detection methods of H_2 are presented [1]. Most of them analyse changes in properties of noble metals like Pd and Pt when exposing to H_2 [2]. Furthermore, alloys of these metals are investigated to find improved properties compared to the pure metals. For example Pd/Ni alloys showed improved sensing properties [3] or Pd/Ag alloys are used for H_2 purification [4].

Alloy investigations in general can be a time consuming task since for each alloy composition one single sample has to be produced and analysed. For binary alloys such investigations are realisable

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whereas for ternary alloys the workload is enormous. Moreover, the catalytic behaviour of alloys is known to be highly nonlinear [4]. Hence, if the steps in concentration variation are too big advantageous compositions might remain unnoticed. Some high throughput screening methods and theoretical analysis are described in literature e.g. for fuel cells [5].

To overcome that situation for catalytic alloys, we developed a high throughput method to investigate different alloys on a single chip. Therefore the light addressable potentiometric sensors LAPS principle was used which is based on the setup described by Hafeman [6]. At first a deposition method to produce continuous gradients in ternary alloys at a single sample was established. The sensor system is similar to an earlier described Pd gate Metal/solid Electrolyte/Insulator/Semiconductor MEIS H_2 sensor [7]. The sensing mechanism is described in detail in [8]. The Pd was replaced with the ternary $Pd_{1-x-y}Ni_xCo_y$ alloy for the high throughput measurements. The measurement system can be called a Continuous Gradient-High Throughput Screening Macroscope CG-HTSM.

In this paper we will demonstrate how the sensor response to H_2 can be locally measured with the LAPS principle and related to the local alloy composition.

2. Experimental

Silicon sensors with an area of 29x29 mm^2 were covered with a homogenous layer of LaF_3 resulting in a $Si/SiO_2/Si_3N_4/LaF_3$ structure see Fig. 1. In a next step a gate metal alloy was deposited by magnetron sputtering in argon plasma using three pure metals (Pd, Ni and Co) arranged on a single sputter source. This leads to a ternary alloy gate with a gradient in the composition. The local alloy compositions were determined by EDX, AES and XPS [9].

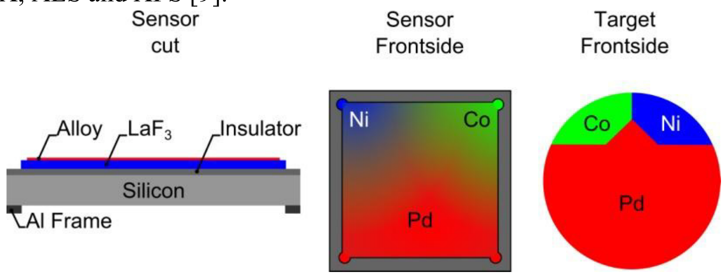


Fig. 1. Sample structure, alloy composition and target configuration for establishing of a ternary alloy with continuous gradient in concentration. The active alloy gate area was 25x25 mm².

For the measurement of the sensor response at the large ternary alloy gate a so called macroscope was build up. Therefore a fibre coupled 1064 nm laser diode was focused with a special f-theta lens (focus spot size 20 µm) to provide a constant focus plane and scanned via a mirror system over the sample. The laser diode was sinusoidal modulated producing an AC photocurrent, which was measured with a lock in amplifier. A LabView program was developed to set the position of the laser focus at the sample, to apply different H_2 concentrations in air *via* mass flow, to analyse the position depending photocurrent. A feedback control was used to determine the potentiometric sensor signal. Typically 25x25 measurement points were analysed in 15 min resulting in 625 different alloy compositions. To determine the H_2 sensitivity different H_2 concentration (10 ppm-30 ppm-100 ppm-300 ppm-1000 ppm in dry synthetic air) were applied. The resulting potential shift E_{H2} against H_2 concentration c_{H2} was fitted with a logarithmic function:

$$E_{H2}=A-B\cdot log(c_{H2}) \tag{1}$$

The sensitivity *B* is given in mV/decade(H_2). As a result the local sensitivity can be displayed over the whole sample.

3. Results

The EDX analysis revealed that ternary alloys are produced with a continuous gradient in concentration, see Fig. 2. The composition can be changed by moving the alloy target across the sample.

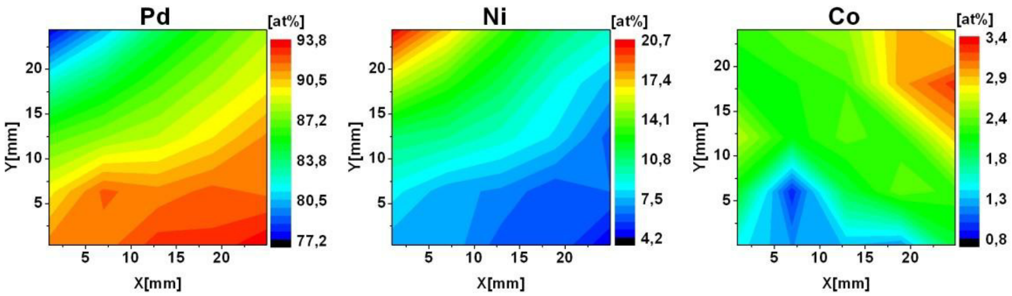
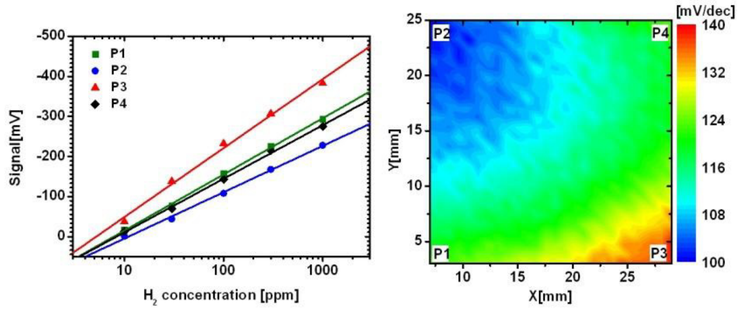


Fig. 2. Alloy composition for palladium, nickel and cobalt as determined by EDX (25 positions)

The alloy gate investigated in the following consists of 77-93 at% Pd, 4-20 at% Ni and 3-5 at% Co. The sensor signal for each of the applied H_2 concentrations was measured with the CG-HTSM at 25x25 sample positions. In the next step the H_2 sensitivity data was fitted for each of the 625 measured positions. Fig. 3a shows the sensor signal at four positions for the H_2 concentrations of 10 ppm-1000 ppm and the fitted linear relation. The H_2 sensitivities for 625 positions are shown in Fig. 3b. The results show that an increase in Ni concentration reduces the H_2 sensitivity of about 40 mV/decade(H_2). The influence of Co is rather small



(a) (b)

Fig. 3. a) Sensor response to H_2 at different positions as indicated in Fig. 3b. b) H_2 sensitivity of 625 measurement points.

With the CG-HTMS the poisoning effect from H_2S at the ternary alloy system was analysed. Therefore, the sensor was poisoned with 100 ppm H_2S in synthetic air for 30 min directly after a first measurement of the H_2 sensitivity. By comparing the sensitivity before and after poisoning one can determine alloy compositions with small influences of H_2S poisoning. In Fig. 4 the difference in H_2 sensitivity is shown. First results suggest that Pd alloys containing Ni between 4-11 at% showed an increased resistivity against 100 ppm H_2S. Areas with such Ni content showed constant or even better H_2 sensitivity after the H_2S poisoning.

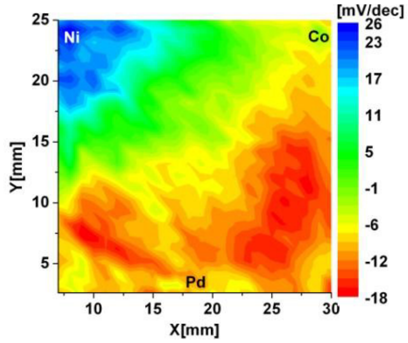


Fig. 4. Difference in H_2 sensitivity after and before poisoning by 100 ppm H_2S at 625 positions (areas with higher Ni, Co and Pd concentration are marked).

4. Conclusions

A new high throughput method Continuous Gradient-High Throughput Screening Macroscope (CG-HTSM) was developed. It was used to analyse ternary $Pd_{1-x-y}Ni_xCo_y$ alloys with a continuous gradient in composition on a single sample. First results showed that Ni reduces the H_2 sensitivity in the range of 4-20 at%. Furthermore, a reduced poisoning effect due to H_2S was demonstrated for Ni a content between 4-11 at%. So far 625 alloys were analysed on a single sample, whereas the CG-HTSM is able to analyse more than 1 million alloys at the same sample.

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