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Sensitivity und Selectivity of Pd-based Thin Film Hydrogen Sensors

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Abstract

Pd-based thin film hydrogen sensors are available on the market since several years. They run due to different physically mechanisms, such as optical switching, changing resistance or capacity of thin film structures. This article describes the capabilities of Pd-thin film optical sensors (POS) and of new micro-electromechanical systems (MEMS). MEMS Pd-based sensors utilise the volume change of Pd due to the hydrogenation, thus they switch mechanically. Both systems detect hydrogen concentrations between 100 vol.-ppm and 100 vol.-% hydrogen in any gas mixtures. They show low cross sensitivities and particularly no cross sensitivity to methane (CH_4) since the switching mechanism is a physical one. The response time (t_{90}) for POS and MEMS sensors is about 20 s and 5 s, respectively. Thus, both sensor types fulfil the requirements of ISO 26142 for control and explosion protection of stationary facilities.

Paper present laboratory investigations of sensory switching of Pd and Pd-alloy thin films deposited by magnetron sputtering. Investigations were conducted on optical transparency for POS and the change in resistance of piezo-electric Si-MEMS structures coated with Pd-thin films. The results show, that the sensory properties can be well explained by the physical properties of the Pd-H System. The absorption of hydrogen in Pd is reversible; it follows the outer partial pressure (Sievert law). The hydrogen initially adsorbed at the Pd-surface diffuse into the metal lattice, an equilibrium concentration of H-atoms in the metal lattice is adjusted. The transparency of Pd and Pd-alloy thin films appears when the solubility of hydrogen in the metallic α phase is depleted and a PdH β-phase occurs. This phase transition in pure Pd occurs at 1,68 at.-% H in Pd [i]. Experimental results revealed that optical sensors with pure Pd-thin films as well as also Pd/Au alloys cannot detect very small H-concentrations, they show the lower detection limit of about 0,1 vol.-%, because the metallic phase is opaque. The transition between the metallic α phase and hydride β phase can be shifted due to intrinsic stress within the ultra-thin Pd – or Pd/Au films [i, ii]. However, the results show that Pd/Y thin films reveal a lower detection limit of about 100 vol.-ppm.

Since the lattice constant in Pd is increasing due to the H-incorporation, the volume change of the Pd-thin films can also be used for sensor switching. The lattice distance within the metallic α phase from pure Pd to 2 at.-% hydrogen is increasing to 3,895 Å and within the β-phase with up to 37,6 at.-% hydrogen it is 4,025 Å [ii]. This volume change is used for MEMS-hydrogen sensors. Investigations revealed a reversible switching of MEMS-Pd-sensors without any drift and fast response for hydrogen concentrations between some 100 vol.-ppm and 100 vol.-% hydrogen. For hydrogen concentrations between 1 vol.-% and 100 vol.-% the t_{90} response time is about 5 s. This volume change also occurs within the metallic α phase and thus MEMS-hydrogen sensors with Pd/Au thin films also detect minimum hydrogen concentrations of about 100 vol.-ppm. The response time for small concentrations is larger, it is about some minutes; however, this is in agreement with data from literature, which report response time increases at lower hydrogen concentrations [iii].

These results show new potentials for hydrogen sensor applications: new application fields for in-situ control of hydrogen concentrations; thus for processes working in high hydrogen concentrations of up to 100 vol.-%, such as in metallurgy, for fuel cells, or chemical process engineering. For low hydrogen concentrations, below the explosive limit, the new sensor concepts particularly show potentials because of their low cross sensitivity. E.g. for breathing gas sensors in medicine technique no cross sensitivity against ethanol or other disinfection liquids are required. Hydrogen concentrations below 150 vol.-ppm in breathing gas have to be detected. Since this concentration range is fare away from explosive concentrations, the longer response time could be acceptable. The most promising and innovative application field for POS and particular for the MEMS hydrogen sensor is the injection of regeneratively produced hydrogen into the natural gas system, as it was demonstrated, that the sensors have no cross sensitivity to methane and MEMS sensors can be produced in a low cost mass production by silicon technology.

Keywords: Palladium optical hydrogen sensor, MEMS hydrogen sensor, detection limits, response time, cross sensitivity

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