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Novel catalytic gas sensors based on functionalized nanoparticle layers

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ABSTRACT

A thermal hydrogen gas sensor with a new type of catalytic layer based on films made of dodecylamine (DDA) capped platinum nanoparticles (DDA capped PtNPs) is presented here. These nanoparticles – prepared by a colloidal synthetic approach – offer, due to their ligand shell, a higher stability and a better adhesion to substrates and show lower agglomeration. Working principle of the sensing elements, consisting of two thermopiles and a central heater placed on a silicon nitride membrane, is the thermoelectric effect. By deposition of the ligand capped nanoparticles on the heated junction of one thermopile, hydrogen can be detected due to a change of the thermopile thermovoltage resulting from the reaction heat released during catalytic H_2 oxidation. A second thermopile was used as a reference element. In order to determine the influence of the organic ligands on the sensor activity, unprotected platinum nanoparticles (unprotected PtNPs) were also used as catalyst. Both approaches, the uncovered and functionalized platinum nanoparticles, have been characterized and exposed to different hydrogen concentrations. Results point towards a strong agglomeration of unprotected nanoparticles resulting in low output signals, whereas for the ligand capped nanoparticles a linear and reproducible output signal with a sensitivity up to 6.4 mV/1000 ppm hydrogen was observed.

1. Introduction

A common application field of hydrogen sensors is sensitive leak alarm systems which are essential when handling with combustible or hazardous gases. Especially, for technical applications e.g. in chemical industry or in hydrogen fuel cells, where hydrogen is used in large amounts, sensitive hydrogen sensors with short response times are of high importance. Another interesting application field for hydrogen sensors is hydrogen breath tests to investigate functional intestinal disorders like fructose or lactose malabsorption as well as the detection of small intestinal bacterial overgrowth syndrome since in these cases hydrogen is exhaled in appreciable amounts [1].

Commercially available hydrogen gas sensors offer a variety of working principles including palladium gated field effect transistors, palladium coated optical fibre type sensors, metal oxide semiconductor (MOS) type and catalytic combustion type sensors [2–4]. So far, most commercial hydrogen gas sensors are of the MOS and catalytic combustion type [5]. Working principle of the latter is a change in temperature of the sensing element, usually a platinum coil, resulting from the reaction heat released during the catalytic combustion of flammable gases [3,4]. The MOS-type sensor is based on a change of conductivity of the sensing material – usually stannic oxide, zinc oxide or titanium dioxide – in presence of reducing or oxidizing gases [3,4].

Both sensor types have several disadvantages i.e. high power consumption resulting from high working temperatures around 400 °C, long response time of several seconds to minutes, poor selectivity due to cross sensitivity to other combustible or reducing gases such as CO as well as a limited concentration range [3,4].

A promising alternative to these sensor types is micro fabricated thermoelectric hydrogen sensor (micro-THS) with nanostructured catalytic materials, i.e. nanostructured platinum [6–8] or palladium thin films [9] as well as platinum nanoparticles supported on Al_2O_3 [10–15]. Similar to the catalytic combustion type sensor the micro-THS is based on the catalytic oxidation of hydrogen over the metallic catalyst, which is placed at one junction of a thermoelectric material. Reaction heat released during hydrogen oxidation leads to a temperature gradient along the thermoelectric component which is translated in a voltage based on the Seebeck effect [6,9–15]. The reaction heat and consequently the voltage are proportional to the hydrogen concentration which leads to a wide detectable concentration range from several ppm up to 3–5 vol.% [7,10,12,13,15]. Response times are stated to range from 2.5 s to 5 s depending on the H_2 concentration [12]. The low size of the sensing device and a highly active catalyst permit a high sensitivity even at low working temperatures down to room temperature. At these low

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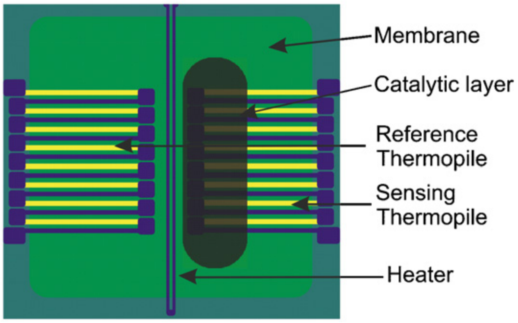

Fig. 1. Schematic view of hydrogen sensor with nanoparticles as catalytic layer.

working temperatures the sensor is highly selective to hydrogen since the catalytic oxidation of other combustible gases such as CO or methane requires higher temperatures [8,13].

Here we present a new type of micro THS based on films made of ligand capped platinum nanoparticles (PtNPs) (Fig. 1). Sensing platform is a thermoelectric flow sensor consisting of a central heater and two thermocouples positioned up- and downstream. One of the junctions of each thermocouple is placed close to the heater on a 600 nm thin membrane of low pressure chemical vapor deposited (LPCVD) silicon nitride while the other junction is placed on the silicon bulk material acting as a heat sink. The membrane is used for thermal isolation of the heater and thermopiles and due to its low thermal capacity a short thermal response time of about 2.6 ms in air can be reached. The thermopiles measure the flow velocity dependent shift in the temperature profile and the resulting sensor signal is a difference of the thermovoltage of both thermopiles [16]. By deposition of PtNPs on the hot junction of one thermopile, the thermal flow sensor is converted into a micro-THS since the reaction heat released during hydrogen oxidation causes a H_2-concentration dependent shift in the temperature profile of the coated thermopile compared to the reference thermopile. This shift in temperature profile leads to a detectable difference of the thermovoltage.

Ligand capped nanoparticles prepared by a colloidal synthetic approach are used as catalytic material, because this type of synthesis offers – in contrast to other synthesis strategies, for example incipient wetness impregnation – a bunch of facilities for controlling structural parameters such as size and shape of nanoparticles which are known to have a strong influence on the performance of nanostructured catalysts [17–19]. A further advantage of the applied synthetic approach is the possibility to attach organic ligands to the nanoparticle surface. While ligands are generally assumed to decrease the catalytic activity because they bind to active surface sites of the catalyst, which are no longer available for the reacting species, several recent studies report a beneficial effect of ligands on the catalyst performance and stability. Most important for catalysts with high metal loadings is the protection against agglomeration and sintering in order to maintain the active catalyst surface. Here, ligands could be considered as distance holders, separating the single nanoparticles and therefore preventing the particles from agglomeration [23,24] even in case of high particle densities (Fig. 3). Although a partial decomposition of the ligands under reaction conditions cannot be fully excluded, it can be presumed that the ligands as well as its carbonaceous residues act as a diffusion barrier preventing the particles from sintering at high temperatures – known to be one of the main reasons of catalyst deactivation [23,25,26] – as has been shown in previous studies [24,27]. Furthermore, Wang and co-workers observed a hydrogenation activity for ligand capped PtNPs supported on SiO_2 superior to that of unprotected PtNPs supported on SiO_2, which was concluded to be due to the protecting effect of the ligands, preventing the particles from surface oxidation [20]. These results clearly demonstrate that, although decreasing the surface area to a certain extent by coordination to active surface sites, the ligand shell can easily be penetrated and the accessibility and catalytic activity of the “uncovered” surface atoms is still given [21,22].

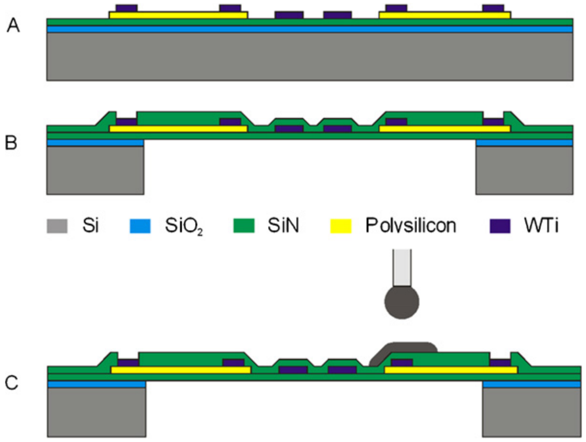

Fig. 2. Fabrication process of the used thermoelectric sensing element: a silicon wafer is covered with thermal oxide and low stress LPCVD silicon nitride. Polysilicon and tungsten titanium are deposited and structured to be used as heating element and thermopile material. (a) Electrical structures are passivated by a second layer of LPCVD silicon nitride and a membrane release is done. (b) Deposition process of PtNPs to be used as catalytic layer (c).

In addition to these protective properties of organic ligands, they offer the possibility of surface structuring, e.g. deposition of the particles on a well defined area of the support [28,29] or they simply improve the adhesion of metal nanoparticles on a given support [27,29].

2. Materials and methods

The thermoelectric sensing element is based on a thermal flow sensor developed by Buchner et al. [30]. A silicon wafer is thermally oxidized and then coated with 300 nm low stress LPCVD silicon nitride later being used as membrane material. The thermopiles are made by a combination of p-doped polysilicon and an alloy of 90% tungsten and 10% titanium (see Fig. 2a). The same alloy of tungsten titanium is used for the heating element. To increase the temperature stability of the thermopiles, a diffusion barrier of titanium nitride is deposited between the polysilicon and tungsten titanium. The high temperature stability is necessary to achieve sufficient thermal stability for the second 300 nm thick LPCVD silicon nitride deposition process. This passivation basically differs from current approaches used for catalytic gas sensing on thin membranes [31]. Characterizations show its higher thermal, mechanical and chemical stability [32] which is an important property for the support of the catalytic layers. Fig. 2b shows the sensing element after removing the bulk silicon from the back by deep reactive ion etching (DRIE). The membrane release made by DRIE has to be done to reduce heat conduction and heat capacity from the functional layers leading to an increase of sensitivity and a decrease of the thermal response time. (For a more detailed description of the sensor fabrication and the role of the low stress LPCVD silicon nitride see Refs. [30,32].) To finish the sensor, the catalyst has to be deposited on one side of the membrane, i.e. close to the heater on the half of one thermopile.

DDA capped and ligand free PtNPs were prepared following the approach described by Wang and coworkers [20,33,34]. To this end, dihydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6{\cdot}6\,H_2O$) dissolved in ethylene glycol (EG) (41 mM; 8.0 g Pt^{4+}/L) was added to an equal volume of a 0.4 M NaOH/EG-solution under stirring