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C-Pd films selective hydrogen sensing in methane presence☆

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ABSTRACT

In this paper we present selective hydrogen sensor for application working in methane presence. Our sensor is based on C-Pd films prepared by physical vapor deposition (PVD) method. The morphology and topography of these films were characterized using SEM and TEM techniques. The sensor evaluation was performed in gas containing different hydrogen concentrations in N_2/CH_4 mixture. For comparison the changes of films response for H_2/N_2 mixture were also measured. It was found that C-Pd films selectively detected hydrogen in the presence of methane in the surrounding atmosphere. Furthermore, CH_4 presence does not affect the kinetics of interaction of hydrogen with the C-Pd films.

1. Introduction

Development and expanded use of hydrogen gas as an energy carrier and as a chemical reactant caused the increasing demand for hydrogen sensors. Gas sensors must be characterized by accuracy, high sensitivity, fast response, high selectivity, low detection limit and low power consumption [1]. One significant disadvantage of many types of commercially available hydrogen sensors is their low selectivity [2]. The demands of future hydrogen economy raise the need for the improvement of selectivity of hydrogen sensors because the selectivity is one of key requirements for gas sensors [2]. The sensing mechanism of many of the applied detectors is based on combustibility or reduction properties of hydrogen gas [3–6]. It implies a possible cross sensitivity to other combustible or reducing gases [2,7–10]. The disadvantage is also consumption of large quantities of energy.

Operation principle of catalytic sensors is based on the fact that reaction of a combustible gas with oxygen on the surface of the catalyst releases heat. This type of sensors exhibits cross sensitivity to other combustible gases such as hydrocarbons and carbon monoxide [2]. Their selectivity can be improved by covering the surface of the catalyst bead with a dense silica layer functioning as molecular sieve [9]. Low selectivity is also shortcoming of electrochemical sensors. They operation is based on changes in charge transport or electrical properties due to electrochemical reactions occurring at a sensing electrode [11]. In addition to hydrogen, electrochemical sensors are sensitive to various hydrocarbons [2]. To reduce their cross sensitivity gas permeable membranes (for example fluorinated ethylene propylene membrane) are used [12]. Such membranes improve selectivity by preventing the diffusion of gases other than hydrogen to the sensing electrode [11]. Another type of detectors is resistance-based semiconducting metal-oxide sensors. Their operation is based on the changes of electrical properties of metal oxides during the exposition to reducing gases. The disadvantage of semiconducting metal-oxide sensors relies on cross sensitivity to other reducing and hydrogen containing compounds such as carbon monoxide, methane, alcohols and humidity [13,14]. To improve their selectivity to hydrogen doping of metal oxides with catalytic metals (*e.g.* Pt, Pd, Au, Ag and Cu) is used [15,16]. Further improvements in selectivity can be achieved by deposition of a thin gas-filtering layer on the surface of the metal-oxide [17].

The most selective sensors are metallic resistors. Their selective hydrogen sensing is based on the specific interaction with hydrogen [2]. An excellent element which highly selectively reacts with hydrogen is palladium. H_2 molecules adsorb on palladium surface and dissociate into atoms which react with Pd forming palladium hydride [18–21]. This reaction causes a change in palladium resistance which can be linked with hydrogen concentration [19–22]. However, the presence of small gas molecules like methane can affect palladium resistance because of their adsorption on its surface [23–26]. Adsorption of methane causes the decrease of palladium resistance due to weak bound complex $(Pd)^-$–$(CH_4)^+$ formation [23,24]. Moreover, methane molecules adsorbed on Pd surface limit the possibility of interaction between H_2 and Pd [27]. CH_4 molecules occupying some of adsorption sites on palladium surface limit the number of the sites on which hydrogen can be

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