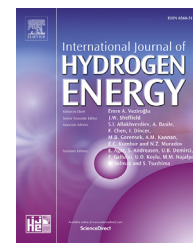


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# Bilayer structures based on metal phthalocyanine and palladium layers for selective hydrogen detection

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## ABSTRACT

In this work, bilayer structures in which a Pd layer was deposited on the surface of palladium phthalocyanine film (PdPc/Pd) by a Metal-Organic Chemical Vapor Deposition technique were studied as active layers of chemiresistive sensors for selective detection of hydrogen. Surface morphology, microstructure and composition of Pd layers were investigated by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. Three sets of bilayer structures with Pd layer thicknesses of 55–80 nm, 100–120 nm and 140–160 nm were obtained to examine the effect of the thickness on the electrical sensor response toward gaseous hydrogen (1–30 v.%). It has been shown that the bilayer structures with 55–80 nm thick Pd layers exhibit the maximal sensor response and can be effectively used for selective detection of hydrogen in the concentration range from 1 to 30% in the presence of gaseous ammonia, CO<sub>2</sub>, NO<sub>2</sub>, and chlorinated alkane vapours.

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## Introduction

Hydrogen is a highly flammable gas and it burns at concentrations as low as 4% in air. Besides, hydrogen has a larger window (4–75%) of flammability in comparison with the natural gas. It is, therefore, critical for a hydrogen sensor to have a wider measurement range (1–99%) for safety applications than for most common fuels [1]. Hydrogen sensors should be not only sensitive to hydrogen over the range of interest concentrations but also selective, i.e. they should be

free of cross-interference from other gases present in the environment.

Several techniques for hydrogen sensing and detection are known; among them several traditional sensing techniques that are still widely used in the industry include gas chromatography, mass spectrometry, catalytic bead (CB), and thermal conductivity [2,3].

Semiconducting metal oxide sensors are also popular solid-state technologies, where heated catalysts are employed to sense hydrogen [1]. These sensors require heating to about 300 °C to enable surface reactions promoting hydrogen

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sensing and therefore can be themselves a potential source of ignition. Electrochemical sensors are based on electrolytic reactions of hydrogen [4]. The most promising solid-state technology is based on a hydrogen-specific material like palladium, among them sensors based on palladium resistors [5,6], palladium field effect transistors [7,8] and optical sensors consisting of a layer of palladium deposited on an optically active material [9].

Surface Acoustic Wave (SAW) devices are also actively used as gas sensors with extremely high sensitivity [10]. A special type of SAW device based on polyvinylpyrrolidone capped palladium nanoparticles (5–20 nm) as a sensing layer was shown to exhibit good sensor response toward hydrogen with the concentration of 0.16% and 8% H<sub>2</sub> in N<sub>2</sub> [11].

The bilayer structures consisted of an organic semiconductor (e.g. metal phthalocyanines) film and Pd layer on a piezoelectric substrate provided one more possibility of detecting hydrogen in a SAW sensor system by using an acoustoelectric coupling between the surface wave and the sensor structure were studied in some works published by Jakubik et al. [12–15]. The layers of phthalocyanines and palladium in these sensor structures were deposited by physical vapor deposition (PVD) technique.

It has been shown elsewhere that metalorganic chemical vapor deposition (MOCVD) technique can be used as the alternative method for forming Pd layers for different purposes [16–18]. Compared to PVD, electrodeposition, and magnetron sputtering techniques, a MOCVD method allows to deposit coatings with smaller grain size and different grain structure [19,20]. An important advantage of a CVD technique is the effective control of the deposition parameters and therefore the structure of deposited layers, viz. crystallites size, thickness, and morphology.

In this work, we prepare and study the structural features and sensor response to hydrogen of the bilayer structures in which Pd layer is deposited by a Metal-Organic Chemical Vapor Deposition technique on the surface of palladium phthalocyanine film. The effect of Pd layer thickness on the sensor response was also examined. It was demonstrated that the electrical resistive sensors on the basis of such bilayer structures possess improved characteristics which are caused by synergistic effect based on a combination of practically important properties of palladium membranes (selectivity to hydrogen adsorption), and metal phthalocyanines (sensitivity of the electrical parameters to the interaction with analytes).

## Experimental details

### Materials

Palladium hexafluoroacetylacetonate Pd(hfac)<sub>2</sub> was synthesized according to the technique described elsewhere [21] by interaction of hexafluoroacetylacetone (1.26 mL, 9.0 mmol) and [Pd(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (1 g, 3.75 mmol) with subsequent purification by vacuum sublimation ( $P = 5 \cdot 10^{-2}$  Torr,  $T = 60$ – $80$  °C). Yield: 1.48 g (76%). M.p. 94–96 °C. Anal. calc. for C<sub>10</sub>H<sub>2</sub>O<sub>4</sub>F<sub>12</sub>Pd, %: C, 23.0; H, 0.3; F, 43.7. Found: C, 23.1; H, 0.4; F, 43.8.

PdPc was synthesized in accordance with the technique described elsewhere [22]. For purification PdPc was sublimed twice in vacuum at a residual pressure of  $10^{-5}$  Torr.

### Films deposition

PdPc layers were obtained by organic molecular beam deposition. The evaporation was carried out at a residual pressure of  $10^{-5}$  Torr with the deposition rate of  $0.6 \text{ nm s}^{-1}$ . During the thin film growth the substrate temperature was held at 60 °C.

Pd layers were deposited by MOCVD technique. The MOCVD experiments were carried out in a vertical cold walls reactor at low pressure (LP-MOCVD), using Pd(hfac)<sub>2</sub> as a precursor. Si(100) slides and Pt interdigitated electrodes (IDE) preliminarily coated with PdPc films were used as substrates. The deposition was carried out at the following experimental parameters: vaporization temperature ( $T_{vap}$ ) was 40–55 °C; substrate temperature ( $T_s$ ) was 130–200 °C; gas-carrier flow rate (Ar) was 1–5 L/h; gas-reagent flow rate (H<sub>2</sub>) was varied from 0.5 to 1 L/h; operating pressure was ~2–4 Torr; the deposition time ( $t_{dep}$ ) was 5–20 min. The MOCVD experimental parameters were selected on the basis of the data of Pd(hfac)<sub>2</sub> thermal properties [23].

### Films characterization

X-ray diffraction patterns were recorded using a Shimadzu XRD-7000 diffractometer (CuK<sub>α</sub> radiation, Ni filter). The patterns were taken in the step-by-step mode in the angular range  $2\theta = 25$ – $65^\circ$ . Surface morphology and cross-section microstructure of layers were analyzed using a scanning electron microscope JEOL–JSM 6700 F. The chemical composition of Pd coatings was determined by X-ray photoelectron spectroscopy (XPS) using a Phoibos-150 SPECS spectrometer (monochromatic AlK<sub>α</sub>-radiation, beam diameter ca 1 mm). Pass energy of an electron energy analyzer was 20 eV. Ion sputtering was carried out using an IQE 11/35 ion source by Ar<sup>+</sup> ions with energy 1 keV at the angle of 45° and the sample current of ~6 μA cm<sup>2</sup>. The sputter analysis was terminated when a steady composition was attained.

### Study of sensor properties

The sensing performance was studied in response to hydrogen (1–30%) diluted in air. Pure commercial H<sub>2</sub> gas was used as an analyte source. The injection of H<sub>2</sub> was carried out at a constant flow rate of 300 ml/min and the exposure time was fixed at 20 s for all examined films. Such a dynamic process rather than a static process was used in order to avoid the irreversible occupation of sites of the active sensor layer as it sometimes occurs when the material is exposed over long durations. This is especially important when high concentrations of the analyte are used. The bilayered structure were deposited onto platinum interdigitated electrodes (DropSens, Spain) to investigate their conductivity changes upon interaction with the gaseous analytes. The dimension of gaps was 10 μm; the number of digits was 125 × 2 with a digit length equal to 6760 μm; cell constant was 0.0118 cm<sup>-1</sup>. The electrical resistance of the films was measured using Keithley 236 electrometer by applying a constant dc voltage of 8 V.

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