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Preparation and properties of carbon-palladium multilayer for hydrogen detection☆

E. Czerwosz [a], P. Dłużewski [b], M. Kozłowski [a, *], S. Krawczyk [a], J. Rymarczyk [a]

[a] Tele & Radio Research Institute, 03-450, Warszawa, Ratuszowa 11, Poland
[b] Institute of Physics PAS, 02-668, Warsaw, al. Lotników 32/46, Poland

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ABSTRACT

The preparation method and some properties of C-Pd multilayered film proper for hydrogen sensing applications are presented. C-Pd multilayered films were obtained by physical vapor deposition (PVD) method by evaporation from of fullerenes (C_{60}) and palladium acetate form two separated sources.

The cross-sectional TEM observations were performed for the samples prepared with the use of focused ion beam (FIB) method. EDX spectroscopy was used to obtained information of the element depth composition of the sample. It was found that the depth modulation of Pd and C concentration is characteristic for all the samples. Simple model of Pd segregation based on diffusion and nucleation explains some features of this multilayers structure.

All studied samples were sensitive to hydrogen.

1. Introduction

The use of metallic thin films for H_2 separation is becoming of increasing relevance for sustainable chemistry and energy. In fact, the increasing demand for hydrogen has raised exponentially the need of new, more efficient processes for H_2 production by hydrocarbon reforming. Steam reforming of natural gas is a well-established technology in refining and fertilizer industries for production of hydrogen.

Pd-based thin films are usually utilized in H_2 sensing and/or permeation processes (e.g. in defect-free membranes). In fact, H_2 catalytically dissociates over Pd and may be transported through the film (membrane) in form of atomic hydrogen, while the transport of other atoms such as oxygen or carbon virtually does not occur. Therefore, it may be possible to selectively separate H_2 from the complex mixtures.

Palladium based materials are able to separate hydrogen selectively because of high solubility of this gas in the Pd crystal lattice. The H_2 permeation mechanism through thin Pd films involves: the dissociation of H_2 to H atoms at the surface of the Pd film, the diffusion of the H atoms across the Pd layer and the recombination of H atoms into H_2 at the opposite surface. This diffusion mechanism is denoted as "solution-diffusion" mechanism since H_2 permeates through Pd by forming a PdH_x alloy [1–4]. Hydrogen transport through a layer of palladium involves different steps: a) adsorption of molecular hydrogen, b) dissociation of the adsorbed molecular hydrogen into atomic hydrogen, c) transport of hydrogen atoms through the bulk of metal via hopping through defects and/or interstitial sites of the metal lattice, d) recombination of atomic hydrogen to molecular hydrogen, e) desorption of the molecular hydrogen [5,6]. When palladium occurs in form of nano- or microstructures the permeability of hydrogen through such nanostructural layer is even better [7,8].

The permeation of hydrogen through carbon film is also good (e.g. for Diamond-Like-Carbon data are in paper [9]). Porous carbon layers or fine-grain graphite layers exhibit high permeability and are stable in high temperatures depending on a permeated gas [10,11]. Current issues with pure carbon layers use as membranes or hydrogen sensitive elements include reduced performance in the presence of strongly adsorbing vapors and the inability to operate in an oxidizing environment [12–15].

In our previous papers [16–19] we showed that nanocomposite carbonaceous-palladium films prepared by PVD method from two

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* Corresponding author.
E-mail address: miroslaw.kozlowski@itr.org.pl (M. Kozłowski).

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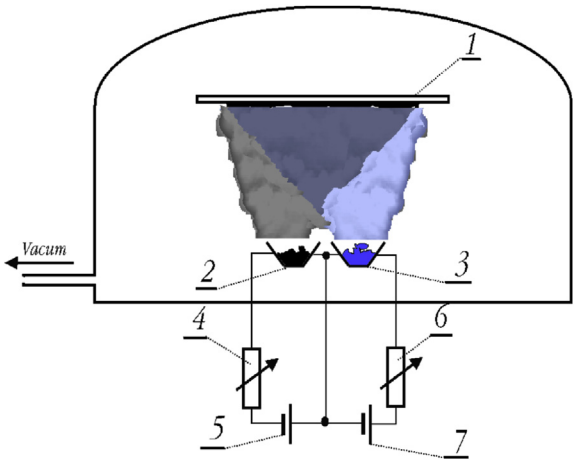

Fig. 1. PVD set-up scheme. Legend: 1 – substrate – quartz plate; 2 – heater source (1) with C_{60}; 3 – heater source (2) with Pd acetate; 4 – control resistor 1; 5 – power supply 1; 6 – control resistor 2 and 7 – power supply 2.

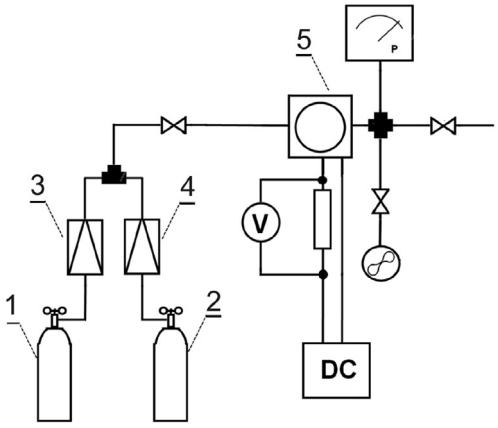

Fig. 3. Experimental setup used for hydrogen sensing measurements (1, 2 – gas bottles, 3, 4 – mass flow controllers, 5 – measurement chamber.

separated sources could be obtained in uniform homogenously form. Palladium nanograins with size of few nanometers are placed in such films in a carbonaceous matrix. This matrix could multi-phase mixture of many allotrope forms of carbon such as graphine plates, fullerite nanograins or amorphous carbon. In this paper we present preparation method and properties of C-Pd films consisting of many very thin layers each with a different structure and Pd concentration. Pd reach layers are built of many very small (few nm in size) Pd grains embedded in carbonaceous matrix. The size and distribution of the palladium grains change from layer to layer causing various properties (such as permeation of solubility of hydrogen) of this particular layer. We show the changes in composition and structure of such layers using EDX spectroscopy connected to TEM observations.

2. Material and preparation method

C-Pd multilayer films were prepared by PVD (Physical Vapor Deposition) method. The process was performed from two separated sources where first source contained powdered fullerite (C_{60}, 99.9% Aldrich) and second palladium acetate (Palladium (II) acetate, 99.98%, Aldrich). The duration time of the process was 10 min at the dynamic vacuum of 10^{-5} mbar. The quartz substrates were applied and the geometry of the element position (sources vs substrates) was as it is shown in Fig. 1. In Fig. 2a,b two types scheme of PVD performing are presented. The temperature of required source was changed gradually every two minutes. In processes of type a) the quantity of initial material in the source was such that after the finished process the rest of material was found in both sources. For the process of type b) we used less fullerite powder and it was not sufficient to be evaporated by the end of PVD process.

The properties of obtained films such as roughness, palladium

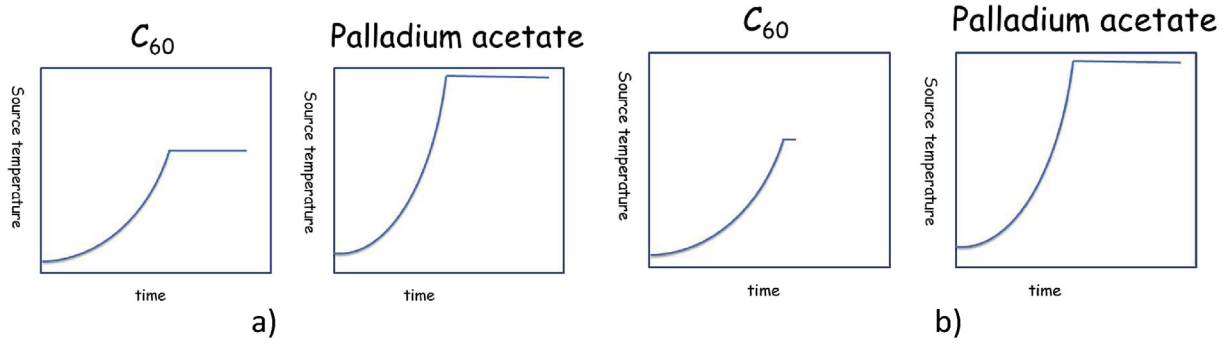

Fig. 2. The schemes of PVD process performing a) type a; b) type b where the fullerite in source is finished and evaporation of this element is finished (substrate temperature vs time changes during the process for each source separately.

Table 1
The properties of prepared film's samples.

	Process type	Temp. Substrate [°C][a]	Ra [nm] (AFM)	N_{Pd} [wt.%]	Resistance[a]	Film thickness [nm]
P1	a	98	3.9	25.2 ± 0.5	7.3 kΩ	400 ± 10
P2	b	90	3.7	32.6 ± 0.7	266 kΩ	380 ± 10
P3	a	90	5.6	17.0 ± 0.7	1.07 MΩ	650 ± 15
P4	a	103	–	25.2 ± 0.5	16.8 MΩ	370 ± 10
P5	a	75	4.4	18.0 ± 0.7	18 TΩ	510 ± 13

[a] The errors for resistance measurements are 10% and for temperature measurements are ±2 °C for all temperatures and are connected to the placement of thermocouple.