Influence of CVD process duration on morphology, structure and sensing properties of carbonaceous-palladium films

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Abstract. We present the nanocomposite carbonaceous-palladium (C-Pd) thin films prepared by physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods. Scanning electron microscope (SEM) and transmission electron microscope (TEM) methods were used to study the topography, morphology and structure of carbon and palladium nanograins contained in these films. The quantitative analysis of the elemental composition of C-Pd films was determined by energy-dispersive spectroscopy (EDS). The initial PVD films were modified in a CVD quartz reactor using xylene (the mixture of isomers) as a modifying factor at different times (5, 10 and 30 minutes) at a constant temperature of 650°C in atmospheric pressure. It was observed that the average size of palladium nanograins increased with an increasing duration of modification process. The differences in microstructures observed in the CVD films modified at different times, affect their response in measurements of resistance changes in the gas containing H₂ in various concentrations. All samples were measured by cathodoluminescence (CL) method. In CL studies a large amount of objects with high intensity of CL was found. Some of them show the emission bands both at 450 nm and 750 nm. Other reveals emission band only at 450 nm. CL observations show that Pd nanograins coated by graphite shells exhibit optical activity.

1. Introduction
Nanostructured materials containing different allotropic form of carbon such as foam, graphite, fullerene C₆₀, nanotubes, nanofibers doped with transition metals e.g. palladium, platinum, nickel, iron, and cooper can be used in various applications e.g. in catalysis, as hydrogen storage materials [1-4], as hydrogen sensors [5-7] or can provide electrodes in batteries [8], fuel cell [9] or can be used as electrochemical biosensors [10]. These materials are characterized not only by highly developed surface area of carbon but also by presence of metals nanograins which play a special role in catalysis. These metals nanograins cause decomposition of chemical compounds adsorbed on them.

Nanostructures based on nanoporous carbon matrix containing palladium nanograins called as the C-Pd films are promising materials for hydrogen sensing applications. Presently hydrogen technologies awaken of great interest among scientists and entrepreneurs. This interest is related to the potential use of hydrogen as an energy carrier. Recently, the growth of the hydrogen importance in the world economy e.g. in transport, chemical compounds production, cryogenic systems, electronic and metallurgical industry has been noticeable.

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Properties such as topography, morphology, electrical and hydrogen sensing of C-Pd films prepared by us, were described in our previous papers [11-17]. One of the factors which decide about using such materials for H₂ detection is presence of Pd nanograins embedded in carbon matrix. On the other hand a well-developed specific surface area of carbonaceous matrix, containing pores with different size and distribution could also play a positive role in hydrogen sorption. Palladium is one of the elements which are capable of reversibly absorbing large amounts of hydrogen [18]. Molecular hydrogen is dissociated at the palladium surface into two H atoms before absorption. Two H atoms can recombine to H₂ in the desorption process. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure–composition isotherms which were presented in papers [19, 20]. The host metal initially dissolves some hydrogen as a solid solution (α-phase). As the hydrogen pressure together with the concentration of H in the metal is increased, interactions between hydrogen atoms become locally important, and start to nucleation and growth of the hydride (β-phase). While the two phases (α and β) coexist, the isotherms show a flat plateau, the length of which determines how much H₂ can be stored reversibly with small pressure variations. In the pure β-phase, the H₂ pressure rises steeply with the concentration.

In this paper we present carbonaceous-palladium films obtained by physical vapor deposition (PVD) method and next modified by chemical vapor deposition (CVD) technology as a potential hydrogen sensitive active layer in the hydrogen sensor. These films exhibit promising solid-gas properties toward hydrogen sorption. Such materials combine physisorption at the carbon pore surface and hydrogenation of the metal forming hydride. The aim of the present work is to study the influence of duration of CVD process on topography, morphology and hydrogen sensing properties of C-Pd films. In order to show difference in the carbon structure and palladium nanograins size in films obtained by CVD modification at different times (5, 10 and 30 minutes) we used SEM, EDS, TEM and CL methods.

2. Experimental

2.1 PVD preparation and CVD modification of C-Pd films

Nanocomposite carbonaceous – palladium films were prepared by physical vapor deposition process. These films were deposited on alumina (Al₂O₃) substrates using as films’ precursors: fullerite C₆₀ powder (99.99%, Sigma-Aldrich) and palladium(II) acetate (Pd(OAc)₂ Sigma-Aldrich). Both compounds were evaporated from two separated sources using electrical heaters. PVD process was carried out in a dynamic pressure of 10⁻³ Pa. The current (I) flowing through the fullerene source was 2.1 A and through palladium acetate source was 1.2 A. Duration time (t) was 8 minutes and distance (d) between sources and substrates was 54 mm. As a result C-Pd films with thickness of 300 nm were obtained what suggesting that the growth rate was 37.5 nm/1min. Next PVD films were modified by CVD method using xylene (the mixture of isomers - Chempure) as an additional carbon source. Xylene was used due to easily decomposition in CVD temperature forming different molecular ions (type: C₃H₅⁺, C₄H₅⁺, C₅H₆⁺, C₆H₆⁺ or C₇H₇⁺ [21]), these ions can react with surface of C-Pd film causing an increase its specific surface area. They additionally form graphite shells around Pd nanograins which were confirmed by TEM method. The expanded surface intensified the reaction with hydrogen.

Process was performed in a quartz reactor at temperature of 650°C in an argon flow rate of 40L/h in an atmospheric pressure. Duration time of CVD modification was varied from 5 to 30 minutes. As the CVD modification result, carbon matrix was converted into porous structures and palladium nanograins appeared on films’ surface. Sample modified by CVD in 5, 10 and 30 minutes was named as S5, S10 and S30, respectively.

2.2. SEM and EDS characterization

The topography, morphology and structure of PVD initial films and films after CVD modification (S5, S10 and S30) was studied by Scanning Electron Microscopy (SEM). These investigations were
performed with the field emission scanning electron microscope JEOL JSM-7600f operating with 5keV incident energy. SEM studies were carried out using two modes of operation: SE (secondary electron) and LABE (low angle backscattered electron). In this mode, the contrast depends on the atomic number of elements of the observed microstructure. Areas with higher atomic number are mapped as bright, while those of lower atomic number - as darker.

The quantitative analysis of the elemental composition of CVD films was determined by energy-dispersive spectroscopy (EDS). The EDS measurements were performed with INCA ENERGY 250 using accelerating voltage of 7 kV with the area scanning method.

2.3. TEM characterization
Transmission Electron Microscopy (TEM) was applied to study structure of S5, S10 and S30 films. The specimens for TEM were prepared by direct moving the C-Pd films from substrate to Cu 1000 mesh grids. The investigation was carried out on JEM 2000EX microscope operating with 200 keV electron beam energy. Electronograms were recorded at fixed camera 600 mm. Observations were performed using a diffraction contrast using technique of bright field – images are formed from the incident beam. The grain size histograms were obtained by considering a region of a sample having about 250 nanocrystals and approximating the shape of each nanocrystal by a sphere. The obtained histograms were fitted to log-normal distributions.

2.4. Cathodoluminescence measurements
Cathodoluminescence measurements were performed on Scanning Electron Microscope Hitachi SU-70 equipped with cathodoluminescence GATAN MonoCL3 system. In measurements were used accelerating voltage of 15kV, photomultiplier as detector and diffraction grating of 300 lines per inch.

2.5. Hydrogen sensing measurements
The sensor evaluation of CVD films was performed in a special measurement set-up. Conductive silver paste (SPI Supplies) was used to make the electrical contacts to these films. These films were placed in the measurement chamber, having electrical feed through, gas flow inlet and outlet. Mass flow controllers were used to ensure a constant, required gas flow rate of 50 ml/min. Hydrogen sensing measurements were performed for different H2 concentration in nitrogen: 0.5 vol.%, 1 vol.% and 2 vol.%. For each hydrogen concentration, three H2 absorption/desorption cycles were performed. The process of hydrogen desorption was carried out in the flow of synthetic air. Measurements were performed at room temperature and under atmospheric pressure.

3. Results and discussion

3.1 SEM and EDS investigations
In figure 1 SEM images in SE mode of PVD films with various magnification are presented. On the film’s surface carbonaceous nanograins are visible. These nanograins have different sizes, posses rounded shapes and smooth walls. Pd nanograins are not observed on film’s surface. According with FTIR investigations the remnant of fullerene C60 and palladium acetate was observed in PVD films [22].
After CVD modification, morphology, topography and structure of PVD films are drastically changed. SE and LABE images of S5 film are presented in figure 2(a, c) and 2b, respectively. As can be seen carbon matrix was transformed into the porous structure, containing on the surface palladium nanograins distributed as evenly. By comparing SE and LABE images it can be seen that Pd nanograins are very fine and are surrounded by graphite shells what was confirmed by TEM method [16]. In some fragments of this film carbon matrix is cracked.

SE and LABE images of S10 film are showed in figure 3(a, c) and 3b, respectively. In this case a greater density distribution of Pd nanograins is observed. Additionally in some areas bigger palladium nanograins are visible. In LABE image around some of Pd nanograins graphite shells are also observed.

In figure 4(a, c) and 4b SE and LABE images of S30 film are showed, respectively. On the film’s surface uniformly distributed very fine Pd nanograins are observed. TEM studies show that these fine nanograins have the graphite shells. It should also be noted that the larger grains with a diameter above
300 nm were found at the boundaries of substrate grains. The larger Pd nanograin were also encapsulated in graphite shells.

EDS analysis was performed at an accelerating voltage of 10 kV at three different areas. In table 1 the average values of the 3 measurements. Since the films thickness does not exceed 200-300 nm, in all cases the Al and O signals recorded from a substrate Al2O3 were registered. It was observed that with an increase in CVD process duration, the films thickness decreased. Therefore, the measured palladium concentration is not a real concentration of this element in all measured films (especially in S30 film which is the thinnest). Thus, the ratio of Pd to C (Pd/C) is more an authoritative indicator comparative. The Pd/C increases with increasing duration of CVD process.

| Elements | S5* | S10* | S30* |
|----------|-----|------|------|
| C        | 73,64 | 69,33 | 65,29 |
|          | 16,46 | 16,46 | 15,02 |
| Al       | 4,68  | 7,41  | 12,23 |
| Pd       | 5,22  | 6,77  | 7,46  |
| Pd/C     | 0,07  | 0,09  | 0,11  |

* All data are given in weight%.

We suggest that reduction of films thicknesss for a longest process is caused by sublimation of remnant of C60 and also an evaporation of palladium acetate. Within the first 5 and 10 minutes is not enough time to the fullerene sublimation occurred (the time may be too short). In case of the longer time in TEM studies we observed, that those Pd nanogrin migrates to the surface films and they connect to the larger grains. The longer time provoke Pd nanograin migration and formation of larger grains.

3.2 TEM characterization

The electron diffraction (ED) pattern is presented in figure 5. All films after CVD modification in various times show the similar electron diffraction pattern. Analysis of ED allows identifying structure of palladium as fcc. In figure 5 the graphite plane {00.2} is also visible. The graphite presence is caused by xylene in CVD process. Our previous studies [16, 17] have showed that annealing of PVD film in argon atmosphere at temperature of 650°C without the xylene presence, did not cause the graphite shells formation. However, in CVD process with the xylene, graphite shells around Pd nanograin were formed.
In figures 6, 7 and 8 we present TEM images and histograms of Pd nanograins size distribution for films modified at 5 minutes (S5), 10 minutes (S10) and 30 minutes (S30), respectively. We observe that the average size of Pd nanograins increases with increasing time of the CVD modification. For S5 film the average size of Pd grains is 42 nm, and for S10 film is 80 nm. Longer time does not significantly increase the size of Pd grains, and for S30 film it is 83 nm. Although in figure 8a in TEM image we can see Pd nanograins with a diameter above 300 nm.

Figure 5 Electron diffraction pattern with identified of the Pd and graphite structure for all S5, S10 and S30 films. The lattice planes of graphite and palladium are indexed.

Figure 6 a) TEM image of S5 film and b) histogram of Pd nanograins size distribution.

Figure 7 a) TEM image of S10 film and b) histogram of Pd nanograins size distribution.
3.3 Cathodoluminescence studies

In figure 9a and 9b, SEM and CL images for S5 film are presented. On CL image 3 objects which emit light are visible. These objects are the palladium nanograins. In figure 9c and 9d CL spectra collected from two objects (top left and right) are showed. In both spectra two wide emission bands are visible. The first emission band with a maximum at 450 nm and the second one with a maximum at 750 nm are observed. It seems that band at 750 nm of the left object is weaker than one of the right object.

In figure 10 SEM and CL images of S10 film are showed. On CL image 2 objects with the luminescence are observed.
Figure 10  a) SEM and b) CL images of S10 film, c) and d) CL spectrum collected from a top left object and a bottom right object.

In both cases emission band at 450 nm is visible, but a bottom right object also shows a strong band at 750 nm.

In figure 11 SEM and CL images of S30 film are presented. SEM image shows a number of objects with different shapes and sizes. These objects vary the intensity of light on CL image. CL spectra were collected from two objects with the highest intensity. The emission spectrum collected from a top left object is very “indistinct” but spectrum collected from a bottom right object shows strong emission band at 450 nm.
Figure 11 a) SEM and b) CL images of S30 film, c) and d) CL spectrum collected from a top left object and a bottom right object.

It results from our previous studies described in paper [16] that Pd nanograins encapsulated with graphite shells are optical active. The shapes and sizes of Pd nanograins may affect the CL spectra and their maxima of emission bands. We suggest that graphite shells may be responsible for the luminescence of Pd nanograins. Further research is required to determine which Pd nanograins have a maximum at 450 nm and which have a maximum at 750 nm. Recently, cathodoluminescence spectroscopy has been used to study the surface plasmon resonance in metallic nanoparticles [23]. According with this paper metallic nanoparticles can absorb and emit visible light due to the surface plasmons.

3.4 Hydrogen sensing of C-Pd films

Hydrogen sensing measurements were performed for S5, S10 and S30 films. The initial resistance of these films measured in air atmosphere is shown in table 2. The films resistance decreased in the function of duration of CVD process. This can be connected with the increase of Pd/C ratio and/or the increase of size of palladium nanograins, what was proved at TEM studies.

| Films | $R_0$ [Ω] |
|-------|------------|
| S5    | $2.14 \cdot 10^9$ |
| S10   | $1.27 \cdot 10^8$ |
| S30   | $7.36 \cdot 10^7$ |

In the sensor evaluation, the C-Pd films resistance was measured continuously during their interaction with hydrogen. For each sample, measurements for 0.5 vol.%, 1 vol.% and 2 vol.% of hydrogen in nitrogen were performed. The investigations were carried out in continuous gas flow. The atmosphere in the measurement chamber was changed every 10 min – H$_2$/N$_2$ and air alternately. The character of changes of samples resistance during hydrogen absorption and desorption was the same for all investigated films. The resistance of all films decreased in hydrogen presence, while the introduction of air caused the increase of films resistance. As a typical result, changes in the resistance of S30 film in 1%H$_2$/N$_2$ are shown in figure 12. Additionally, in the right axis of figure 12 the changes of sensitivity versus time are shown. The sensitivity to hydrogen is defined as the percentage change in film resistance. The sensitivity ($\Delta R/R_0$) was calculated using the following equation:

$$\Delta R/R_0 = \frac{R - R_0}{R_0} \cdot 100\%$$  \hspace{1cm} (1)

where R - film resistance after exposure to H$_2$, $R_0$ - film initial resistance in H$_2$ absence.
The sensitivity of the studied films varied depending on time of CVD process. It also depended on hydrogen concentration. In figure 13 the sensitivity of S5, S10 and S30 films in the function of hydrogen concentration is presented. These values were calculated after 2 min from introduction of hydrogen. As one can see, the highest sensitivity characterized the film modified in 30 min, while the lowest one was observed for S5 film for all studied H₂ concentrations. This means that the application of the longest duration of CVD process led to obtaining of the film with the best hydrogen sensing properties.

**Figure 13** The sensitivity of S5, S10 and S30 films as a function of H₂ concentrations

4. Conclusion

In this work we present the carbonaceous – palladium films after modification by CVD method using various time. We studied the influence of duration of CVD process on morphology, topography and structure of the carbonaceous matrix and shapes and sizes of palladium nanograins. We observe that with increasing duration of CVD modification, the thickness of films decreases but size of palladium nanograins increases. Resistance of film with the smallest thickness is the lowest. This result can be caused by the presence of bigger Pd nanograins with a diameter above 300 nm, which may touch each other in some areas on film’s surface. Investigations of hydrogen sensing properties show that film modified in 30 minutes has the highest sensitivity and can be used as an active layer in hydrogen sensor.
In TEM and SEM studies palladium nanograins encapsulated in graphite shells were found. These Pd nanograins showed emission bands with maxima at 450 and 750 nm. We suggest that the graphite shells are responsible for the optical activity of Pd nanograins.

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