Preparation of nanocomposite carbonaceous films containing palladium nanograins and studies of the annealing time influence on their structure and sensing properties

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Abstract. C-Pd films were obtained by Physical Vapor Deposition (PVD) or by annealing of these initial PVD films at 650°C in different time (5, 10 and 30 minutes) in argon flow. These C-Pd films were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and FTIR spectroscopy. The sensing properties of the films were studied in a specially prepared chamber allowing for measurements of the changes in resistivity as a function of gas composition changes. It was found that annealing changes the films morphology, topography and structure, and consequently their sensing properties.

1. Introduction

Since Seiyama [1] developed the first solid-state gas sensor, many other research groups have been attempting to improve gas sensors, with the aim of enhancing their sensing performance. Many materials such as: carbon nanotubes, nanoporous carbon, diamond-like carbon, graphene can detect low concentrations, of ppb order, of gases such as NO₂, NH₃, O₂, H₂, CO₂, and CO [2–8]. However, there are carbonaceous materials with very high resistivity 10⁷–10⁹ Ω·cm [9,10] that can be applied for sensing different gases by such resistivity limit their sensitivity. Introduction of nanoparticles or nanograins of some metals improves sensing properties. For instance, introduction of palladium nanoparticles into a carbonaceous film allows obtaining a very sensitive hydrogen sensor [11-14]. This phenomenon is connected to solubility of hydrogen in palladium lattice [15-17]. It is known that nanostructural Pd materials improve H₂ sensing in comparison with metallic palladium. In the presence of H₂ the resistivity of Pd will change due to the formation of a solid solution of Pd/H [18]. Furthermore, Pd is highly selective to H₂. Several fundamental problems are associated with bulk Pd-based hydrogen sensors. First, the diffusion of the hydrogen into bulk Pd, e.g. thick Pd film, can cause a large internal stress destroying the film irreversibly [19, 20]. Second, at room temperature the hydrogen atoms diffusion in Pd is very slow (the diffusion coefficient is 3.8 × 10⁻⁷ cm²/s at 298 K [21]) what causes long time of response for hydrogen. Now, palladium nanomaterials development leads to production of new class of H₂ sensors. These sensors could base on single Pd nanowires [18, 22-24] or on thin films containing nanograins of Pd [25-27]. These films can be obtained by different method (atomic layer deposition, physical vapor deposition or chemical vapor deposition). The change...
of their resistivity due to hydrogen absorption/desorption is a measure of their sensitivity toward hydrogen. They give promising results taking into account response time, sensitivity and ultralow power consumption.

In our previous papers [11-14, 26-29] we have presented the results of structural, morphological and sensing studies of film composed of nanograins of palladium placed in a carbonaceous matrix. These films were prepared on different substrates (Si, porous Si, Al$_2$O$_3$ ceramic) by physical vapor deposition (PVD) method. The changes of the film structure and composition could be controlled by technological parameters. We can also control the size and distribution of Pd nanograins, Pd content in the film and film resistivity. These films exhibited high sensitivity to hydrogen, fast response and selectivity for hydrogen sensing. In this paper, we present the results of studies of the influence of annealing of these films on their sensing properties. Films obtained by PVD method were annealed at 650°C in an argon atmosphere for different time. We found that annealing of non-conductive C-Pd films could lead to the film structure changes causing change of its conductivity. Conductive paths based on palladium nanograins are formed in these C-Pd films. The sensitivity of these films to hydrogen was also discussed.

2. Experimental

The nanostructural C-Pd films were prepared by PVD (Physical Vapor Deposition) from two separate sources containing: fullerene (first) and palladium acetate (second). In this process, performed in dynamic vacuum with the pressure of 10$^{-6}$ mbar, films were obtained by deposition of fullerene C$_{60}$ (Sigma-Aldrich, 99.9%) and palladium acetate Pd(OAc)$_2$ (Sigma-Aldrich, 99.98%). These films were deposited on Al$_2$O$_3$ substrates, with the deposition time $t = 10$ min. The roughness of the substrate was 0.13-0.2 μm. Currents through both sources were the same for all prepared films. The distance $d$ between the sources and the substrate was changed and it was 54 mm for sample S1 and 69 mm for S2. This caused a small difference of temperatures on the substrates: $T=59$°C for S1 and $T=54$°C for S2 and bigger difference in Pd content (see Tab.1). The temperature of substrate was measured during all PVD process and given here temperature is the final temperature registered and the final moment of this process. It should be noticed that temperature for both PVD processes (for sample S1 and S2) stabilized after 4-5 min from the beginning of the process. The temperature was measured with thermocouple fixed always at the same place of the sample. These measurements were repeated several times to estimate the errors connected to the method of thermocouple mounting and heating time of sources. Films prepared by PVD were annealed at 650°C. The annealing was performed in argon atmosphere (to prevent oxidation of palladium), in three different time values: 5, 10 and 30 minutes. The films annealed at different time are marked as S1A(5/10/30) and S2A(5/10/30).

The palladium content in the initial films obtained by PVD was determined by atomic absorption spectra for a proper solutions of films prepared by wet chemical analysis.

The resistivity of PVD initial films was measured in an experimental set-up, prepared for testing a gas influence on electrical properties of films (Figure 1). The changes of the electrical resistivity of C-Pd films at 1%H$_2$/N$_2$ mixture of gases were measured under room conditions (temperature and pressure). The flow rate of 1%H$_2$/N$_2$ gaseous mixture was kept constant and it was 50 ml/min. After absorption of hydrogen, the air was introduced (with a rate of 50 ml/s) to the experimental chamber to remove H$_2$ gas. Several hydrogen absorption-desorption cycles were carried out for each sample. After desorption, the resistance reached the final value after 30 minutes and remained stable afterwards. It should be mentioned that obtained in this way the response of the film for hydrogen cannot be used for determination of real response time, that is the immediate response of film to contact with gas. In this experiment we register time of total exchange of gas and air in experimental chamber.
Figure 1 A) Experimental setup for sensing measurements (1, 2 – gas bottles, 3, 4 – mass flow controllers, 5 – gas mixer, 6, 10, 11 – valves, 7 – measurement chamber, 8 – pressure meter, 9 – four-way splitter, 12 – vacuum pump, 13 – voltmeter, 14 – reference resistor, 15 – voltage source, 16 – temperature controller). B) Photo of the measurement chamber.

Technological parameters, concentration of Pd and resistivity of initial PVD films and annealed films are gathered in Table 1.

Table 1. Technological parameters, concentration of Pd and resistivity for C-Pd films

| Sample number | \(d\) [mm] | Pd content [wt %] | Annealing time [min] | Resistivity \([10^6 \Omega \cdot \text{cm}]\) |
|---------------|------------|-----------------|----------------------|------------------|
| S1            | 54         | 17              | >60                  |                  |
| S2            | 69         | 10              | >60                  |                  |
| S1A5          |            | 5               | >60                  |                  |
| S1A10         |            | 10              | >60                  |                  |
| S1A30         |            | 30              | >60                  |                  |
| S2A5          |            | 5               | 29.9                 |                  |
| S2A10         |            | 10              | 21.9                 |                  |
| S2A30         |            | 30              | 6.1                  |                  |

The films were also characterized by Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). SEM investigations were performed with the use of JEOL JSM-7600F electron microscope with a Secondary Electron (SE) detector and with a Low Angle Backscattered Electron (LABE) detector. LABE mode is used to present a contrast composition of the film components (C and Pd). The field emission SEM was operated at 5 keV incident energy. TEM investigations and electron diffraction from a selected area (SAED) were performed for some selected samples. These investigations were performed with JEOL JEM-2000EX electron transmission microscope operating at 200keV incident electron beam energy.
FTIR spectra were obtained with ThermoScientific Nicolet iS10 FTIR spectrometer, using Attenuated Total Reflectance (ATR) in the spectral range of 650-4000 cm\(^{-1}\), at the spectral resolution of 4 cm\(^{-1}\).

3. Results and discussion

3.1. PVD C-Pd films

Neither S1 nor S2 films were sensitive to hydrogen, while analyzing their resistivity changes in a hydrogen presence.

Initial films prepared by PVD method contain 10 and 17 wt. % of Pd. The resistivity of these films was very high (>6x10\(^7\) Ω·cm) and did not change when the films were introduced into the chamber filled with a H\(_2\)/N\(_2\) mixture. Such high resistivity could be attributed to palladium nanograins distribution in a carbonaceous matrix. This is shown in TEM images for samples S1 and S2. In Fig. 2a and Fig. 3a TEM images of S2 and S1 samples are presented, respectively. Pd nanograins are seen as dark objects. These Pd nanograins are rarely distributed and they cannot form conduction paths, even when PdH\(_x\) grains are formed. In TEM image presented Fig. 2d one can see the area with fullerene molecules forming fullerite with fcc type structure. In this image the distance d\(_{111}\) for this structure is marked. In Fig. 2b and Fig. 3b selected area electron diffraction (SAED) patterns from the fragments of films are shown. The SAED pattern for the sample S1 consists of diffuse rings with the low diameters, related to diffraction on very small amorphous carbonaceous grains and diffraction rings, and with large diameters attributed to very small Pd nanograins. The Pd nanograins size distribution analysis for sample S1 shows that the diameter of nanograins is between 4 and 16 nm (see diameter size distribution histogram in Fig. 3c). The SAED pattern for sample S2 is different and contains diffuse rings that could be attributed to diffraction on C\(_{60}\) fullerite nanograins (internal rings) and reflexes related to diffraction on large Pd grains. These nanograins sizes can be determined from size distribution histogram and they are 5-100 nm.

![Figure 2 a) TEM image for sample S2; b) SAED pattern for S2; c) Pd nanograins size distribution for S2, d) TEM image of the area with fullerite structure](image-url)
S1 and S2 films have similar molecular structure, which is confirmed by FTIR spectra (Fig. 4). Bands marked with arrows can be attributed to the vibrations of $\text{C}_60$ molecule and C-O groups in palladium acetate. For a comparison spectra of fullerene and palladium acetate are also presented. Based on these spectra we can deduce that palladium acetate molecules or clusters of molecules are present in films. It should be mentioned that the carbonaceous matrix is non-conductive when is based on fullerenes molecules. Decomposition temperature of Pd acetate is much lower (210-290 °C) than final temperature of source (800-1100 °C) containing Pd acetate. For some experiments (with low heating ratio), the temperature of the source containing acetate is low during the first moment. Then, palladium acetate could not be decomposed completely and this could be a reason why in FTIR spectra we can observe a trace of Pd acetate. When the heating ratio is high enough no trace of acetate should be observed.

SEM images of samples S1 and S2 are similar and they show that the film topography is dominated by the substrate surface shape (big grains of one or a few μm in size). Oval grains with the diameter of ~200-300 nm can be observed on these grains. The example of a typical topography of these samples is presented in Fig. 5a and b. We did not observe Pd nanograins even at the highest resolution of SEM images. Non-conductive character of samples made difficult obtaining a sharp image at the highest magnification.
3.2 Annealed films

S1 and S2 film after annealing under the same conditions reacted with hydrogen in a different way. S1 film annealed for 5, 10 and 30 minutes did not change its resistivity in the presence of hydrogen. S2 annealed samples changed their resistivity (decrease) and they were highly sensitive to hydrogen. In Fig. 6 are presented the resistivity changes due to interaction with a 1% H$_2$/N$_2$ gas mixture.

![Figure 6 Changes of resistivity in 1% H$_2$/N$_2$ for the following samples: a) S2A5, b) S2A10 and c) S2A30.](image)

SEM and TEM images of samples S1A5 and S1A10 are shown in Fig. 7. The grains of palladium are of different size (up to a few hundreds nm) and they are randomly distributed on the sample surface. The agglomeration of small palladium nanograins increases with the annealing temperature and for S1A30 sample leads to the growth of very long Pd grain (a few μm). Most of Pd grains are small and the carbonaceous matrix seems tight. SAED patterns
prove an amorphous character of the matrix. These amorphization of carbonaceous matrix is due to catalytic reaction of palladium with this matrix undergoing in high temperature. These diffraction patterns also exhibit reflexes related to the Pd fcc crystalline type structure (Fig. 7d).

![Figure 7 SEM images of samples S1A5 and S1A10: a) SE image and b) LABE image for S1A5, c) SE image for S1A10 and d) SAED pattern from S1 annealed film. Bright objects in SEM images are palladium grains.](image)

Fig. 8 presents SEM images of S2 film annealed for 5, 10 and 30 minutes. For all these samples we observed the effect of formation of conductive paths composed of palladium grains collected on the Al₂O₃ grains border. For samples S2A5 and S2A10 the form of such a conductive path is similar and Pd grains packing along the path is similar. For sample S2A30 it seems that Pd grains do not form the paths, but they are uniformly distributed in all volume of the film. The carbonaceous matrix has a porous form for all these samples. More pores are formed as the annealing time increases (Fig. 9a-c). The diameter of the pores decreases with the increasing annealing time. Palladium grains are placed in these pores and form a very dense network of connections. Palladium grains placed in the pores are the smallest in sample S2A30. This effect could cause lowering of the resistivity of this sample. During the films interaction with hydrogen the volume of palladium grains increases and the network of these grains becomes more effective, because of a closer contact between them. This effect could have a stronger impact to the film conductivity than the effect of PdHₓ formation, which reduces the film conductivity due to PdHₓ resistivity being higher than the resistivity of palladium. This mechanism could be responsible for the observed decrease in the film resistivity in the presence of hydrogen.

The film porosity could also affect its resistivity. It was demonstrated [30] that the resistivity of porous carbon material is \(\sim 10² - 10³ \ \Omega \cdot \text{cm} \) and decreases as the temperature goes up. The combination of these two above mentioned effects could also diminish resistivity of film. However the porous carbonaceous structure could play a role in hydrogen absorption and hydrogen-carbon stable bonds could be formed, which results in lowering the baseline during hydrogen sensing measurements (Fig. 6c). Such resistivity changes during sensing measurements are connected with non-total desorption of hydrogen from the film.
Figure 8 SEM images of S2 film annealed in argon for a,b) 5, c,d) 10, e,f) 30 minutes. Bright objects are palladium grains.
4. Conclusions

In conclusion, annealing of C-Pd films in argon causes an improvement in the sensing properties for films with 10 wt% of Pd. Annealing of such non-conductive C-Pd films obtained by PVD method could improve their conductivity due to a formation of Pd nanograins conductive paths and a porous carbonaceous matrix. Annealing allows for such modification of the structure of C-Pd films that leads to the formation of palladium conductivity paths and formation of a network of palladium nanograins placed in the pores of the carbonaceous matrix.

The film containing less Pd seems most suitable for application in hydrogen sensors. Annealing of PVD films at different time improves their initial sensing properties (response time lower than 100 s, low noise to signal ratio, high response value).

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