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INFLUENCE OF CVD PROCESS DURATION ON MORPHOLOGY, STRUCTURE AND SENSING PROPERTIES OF CARBONACEOUS - PALLADIUM FILMS

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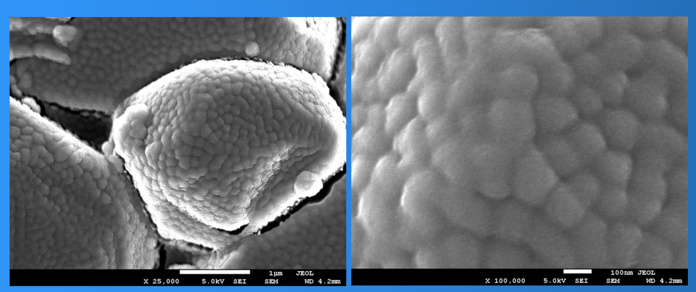
Nanostructured materials containing different allotropic form of carbon such as foam, graphite, fullerene C_{60}, nanotubes, nanofibers doped with transition metals (Pd, Pt, Cu, Fe, Ni) can be used in various applications e.g. in catalysis, hydrogen storage materials, hydrogen sensors, as electrodes in batteries or in fuel cell. 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 word economy e.g. in transport, chemical compounds production, in electronic and metallurgical industry has been noticeable.

We present C-Pd films based on nanoporous carbonaceous matrix containing Pd nanograins which are promising materials for hydrogen sensing applications. These films were prepared by PVD method and next were modified in CVD process at different times (5, 10 and 30 minutes). The aim of this work is to study the influence of duration of CVD process on morphology, topography, structure and hydrogen sensing properties of these films. These films are deposited on alumina (Al_2O_3) substrates and can be used as an active layer in hydrogen sensor.

SEM studies of PVD film



SEM images show boundaries of substrate grains. On substrate surface carbonaceous nanograins are visible. These nanograins have different sizes, posses rounded shapes and smooth walls.

After CVD modification morphology, topography and structure of PVD film are drastically changed.

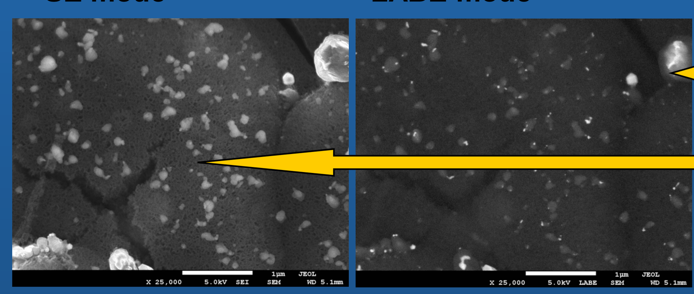
Parameters of CVD process

Sample	Temp. [°C]	Feed of xylene [ml/min]	Time [min]	Argon [L/h]
S5	650	0,1	5	40
S10	650	0,1	10	40
S30	650	0,1	30	40

SE and LABE images of CVD films

Secondary Electron Low Angle Backscattered Electron

SE mode **LABE mode**

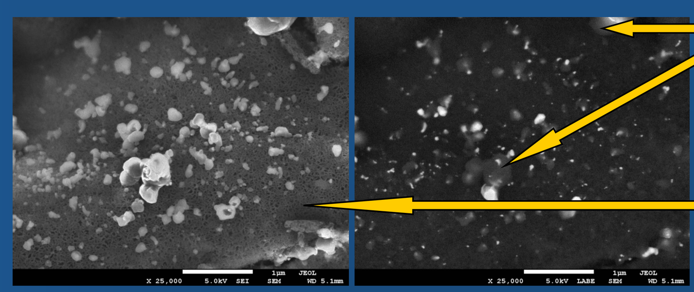


Graphite shells around Pd nanograins

Porous carbon structure

Pd nanograins are uniformly distributed

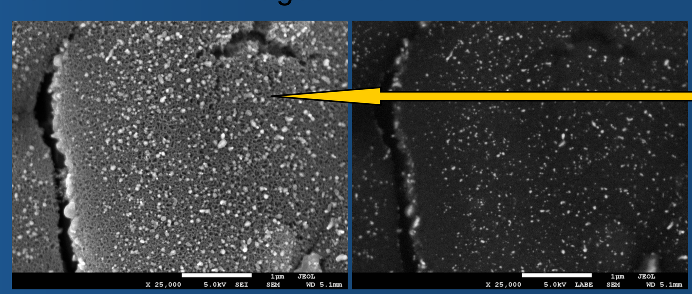
SE and LABE images of S5 film



Pd nanograins encapsulated in graphite shells

Porous carbon structure

SE and LABE images of S10 film

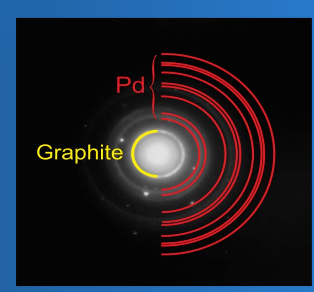


Very fine Pd nanograins are uniformly distributed. TEM studies confirmed that these fine nanograins have the graphite shells

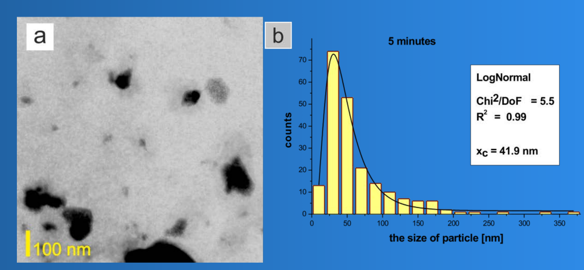
The larger Pd grains with a diameter above 300 nm were found at the boundaries of substrate grains. These Pd nanograins have also graphite shells

SE and LABE images of S30 film

TEM image of CVD films

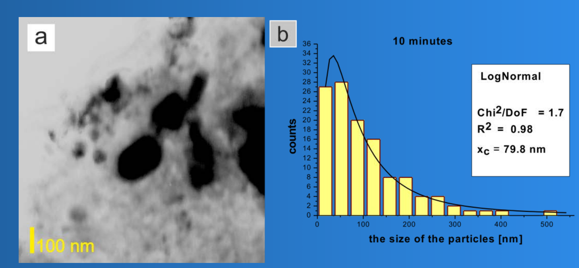


Electron diffraction (ED) pattern with identified of Pd and the graphite structure. All films after CVD modification have the same ED pattern



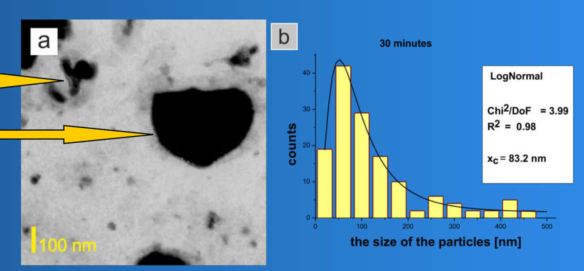
TEM image and the histogram of Pd nanograins size distribution in S5 film

The average size is 42 nm



TEM image and the histogram of Pd nanograins size distribution in S10 film

The average size is 80 nm



TEM image and the histogram of Pd nanograins size distribution in S30 film

The average size is 83 nm

Hydrogen sensing of C-Pd films

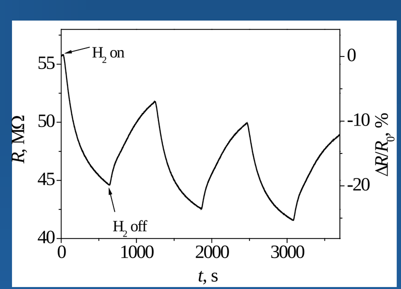
Hydrogen sensing properties were performed in different concentration of H_2/N_2 (0.5vol.%, 1vol.% and 2vol.%). The resistance changes of all films were carried out in the special chamber. The films' resistance decreases in hydrogen presence.

The sensitivity ($\Delta R/R_0$) was calculated using the following equation:

$$\Delta R / R_0 = \frac{R - R_0}{R_0} \cdot 100\%$$

where R - film resistance after exposure to H_2

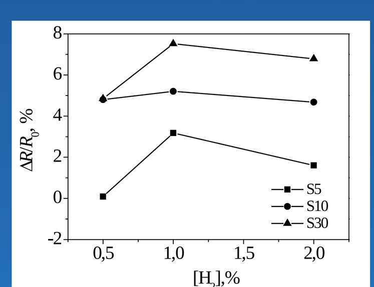
R_0 - film initial resistance in H_2 absence



The resistance changes of S30 film in mixture of 1%H_2/N_2

Resistance of C-Pd films in air

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



The sensitivity of S5, S10 and S30 films as a function of H_2 concentration

Film modified in 30 minutes has the highest sensitivity

This film characterizes the smallest thickness and the largest Pd nanograins and the greatest ratio of Pd/C, thus it can be used in hydrogen sensor applications

EDS measurements

Energy-Dispersive Spectroscopy

EDS analysis of S5, S10 and S30 films

Elements	**S5**	**S10**	**S30**
C	73,64	69,33	65,29
O	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 %

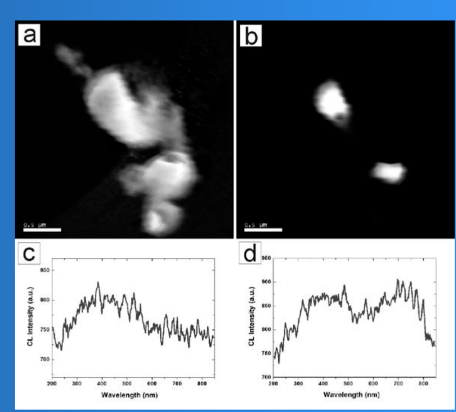
Al and O signals originated from the substrate Al_2O_3

The thickness of the films decreases with increasing time of CVD modification.

The smallest thickness has film modified the longest.

The ratio of Pd/C increases with increasing duration of CVD process.

Cathodoluminescence studies



SEM (a) and CL (b) images are presented for S10 film

On CL image 2 objects showing luminescence are visible. The object placed on top left shows maximum only at 450 nm, but object placed on bottom right shows two maxima at 450 nm and at 750 nm. Emission band at 750 is very strong.

Conclusion

- duration of CVD process influences on morphology, topography and structure of carbonaceous matrix and also Pd nanograins in films prepared by PVD process;
- with increasing duration of CVD process the films' thickness decreases;
- with increasing duration CVD process the size of Pd nanograins increases;
- the ratio of Pd/C increases with increasing time of CVD process;
- the film with the smallest thickness has the highest sensitivity and can be used as an active layer in hydrogen sensor;
- Pd nanograins encapsulated in graphite shells are optical active and show emission bands with maxima at 450 and 750 nm

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