SMART MATERIALS FOR HYDROGEN and RENEWABLE ENERGY
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PD-C NANOFILMS FOR HYDROGEN SENSORS

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Introduction

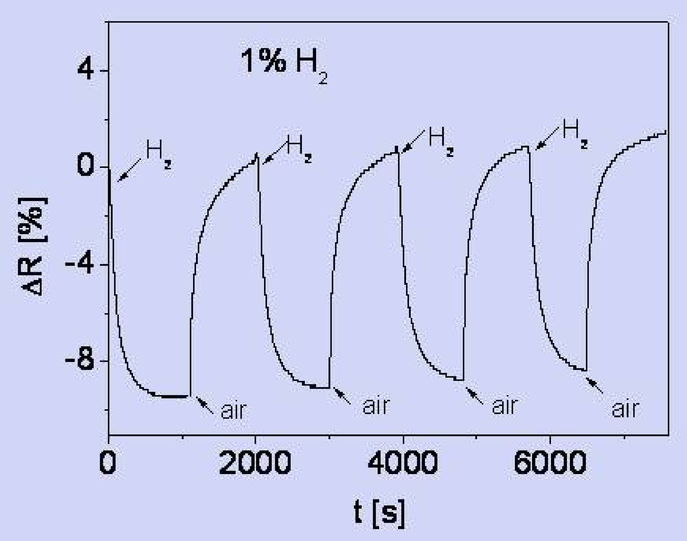
Palladium is an ideal material for hydrogen sensing because it selectively absorbs hydrogen gas and forms a chemical species known as a palladium hydride. Hydrogen sensor design rely on the fact that electrical resistance of palladium hydride is greater than the resistance of pure Pd. Absorption of hydrogen in such materials is accompanied by a measurable increase in electrical resistance [1].

Our Pd-C film sensor is based on an opposing property that depends on the Pd nanograins sizes and their distribution in carbonaceous matrix. In this film, nanosized palladium particles swell when the hydride is formed, and in the process of expanding, some of Pd nanoparticles form new electrical connections with their neighbors [2]. The increased number of conducting pathways results in an overall net decrease in resistance. Depending on the structure of carbonaceous matrix (porous or amorphous carbon) and size and distribution of Pd nanograins in these films we can observe first or second type of changes undergoing due to hydrogen absorption.

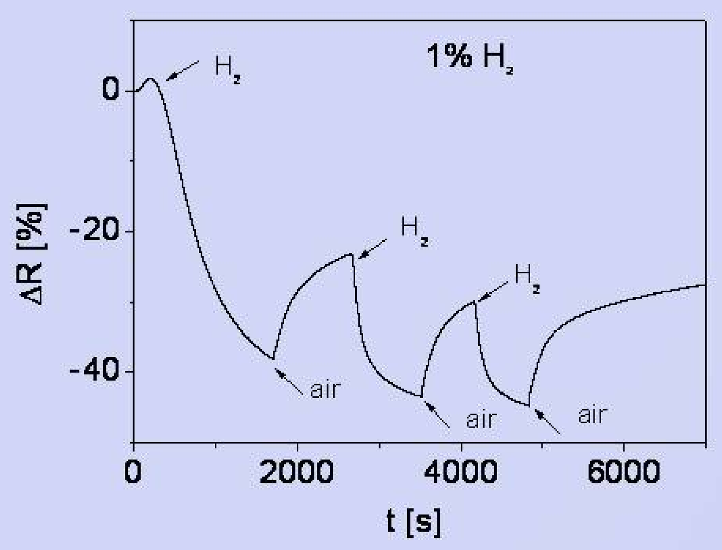
Characterisation of films

All films are fully characterised by:

- Transmission and Scanning Electron Microscopy – for studies of structure and topography of films
- Fourier Transformed Infrared absorption spectra – for studies of decomposition of components of PVD process
- X-ray diffraction – for studies of Pd grains structure
- Measurement of resistance changes observed during hydrogen absorption – for final selection of films sensitive to hydrogen



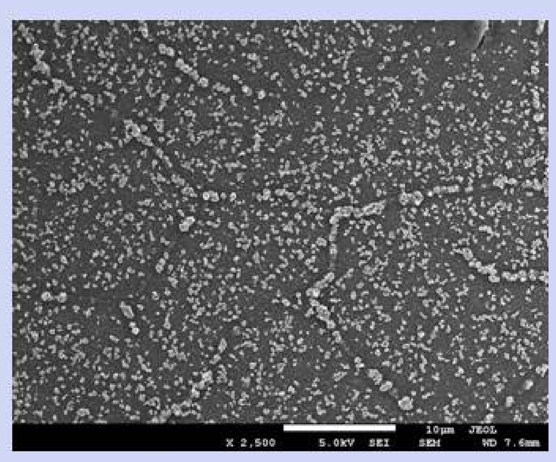
Typical response for hydrogen of film of type 3



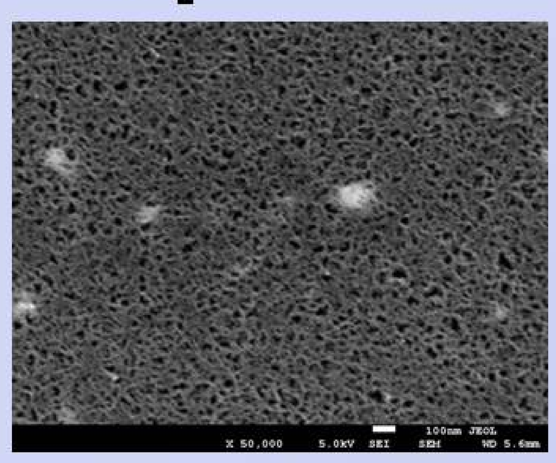
Typical response for hydrogen of film of type 1

Types of films on different substrates:

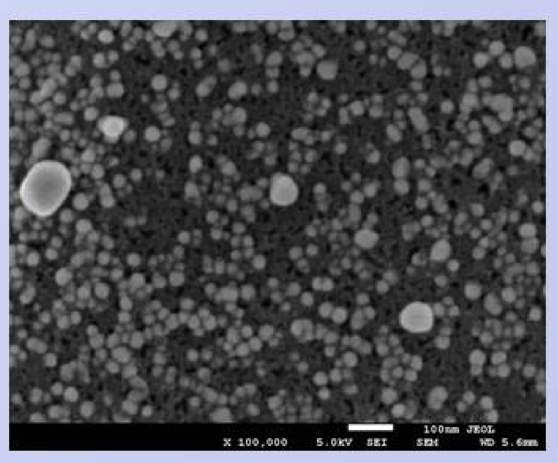
Fused silica



SiO_2/Si



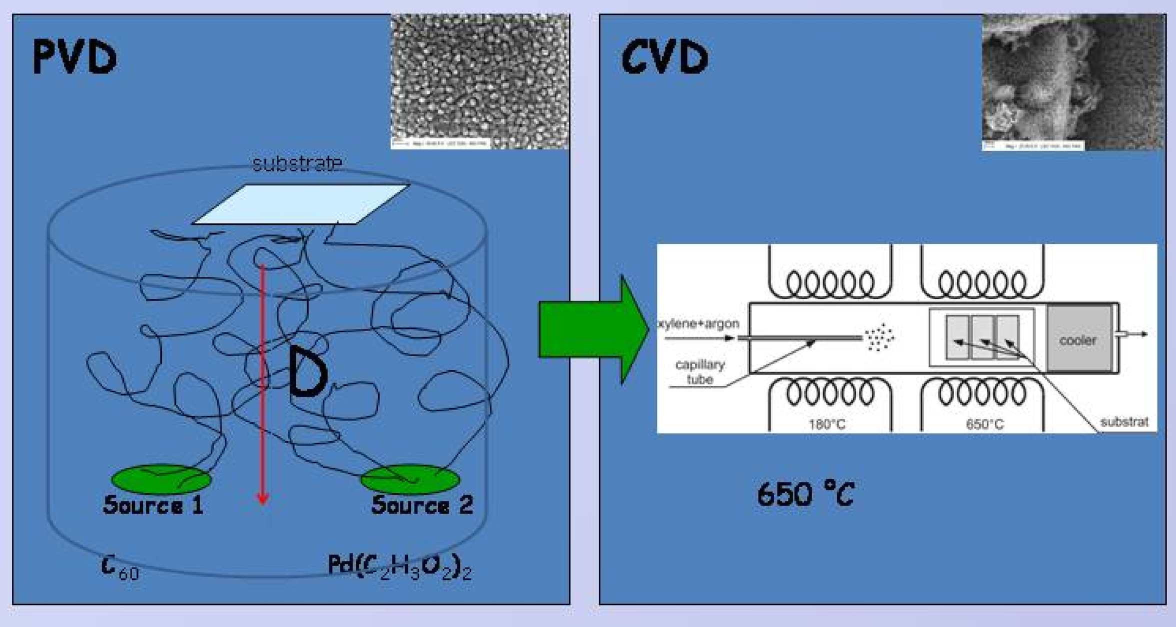
Mo foil



Depending on the substrates' type the different C-Pd nanostructures are observed. These differences are caused by a thermal conductivity of materials used as the substrate. In case of fused silica, carbon matrix has amorphous structure and numerous Pd nanograins are deposited on its. Carbon matrix is porous like foam in both SiO_2/Si and Mo foil substrates but on Mo definitely more Pd nanograins are dispersed with more regular shape.

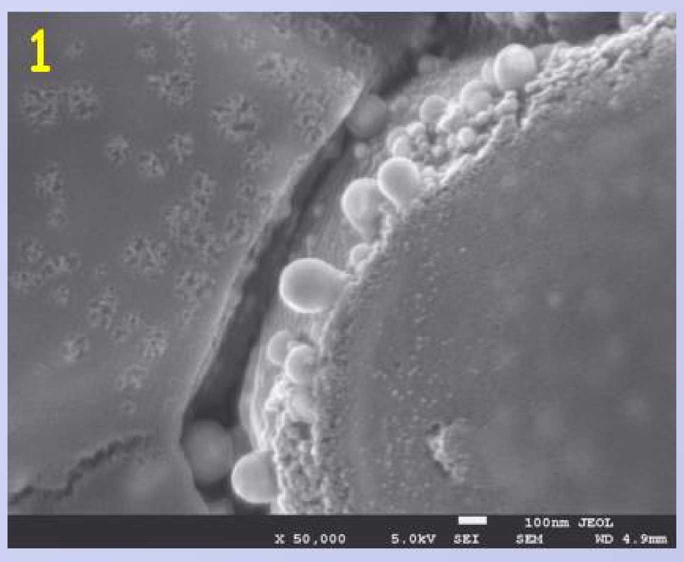
Technology

The nanostructural C-Pd films were obtained by Physical Vapor Deposition (PVD) method and next they were modified by Chemical Vapor Deposition (CVD) process. In PVD process two separated sources containing fullerene C_{60} and palladium acetate $Pd(OAc)_2$ were used to prepare the initial films. The parameters of PVD process such as sources temperature (or current through these sources), sources-substrate distance and duration time of the process influence on the structure and thickness of deposited film. CVD process with xylene as additional carbon's source was carried out in argon flow. CVD process temperature, xylene feed rate, and time of duration of the process are reflected in the final form of Pd-C film.



Types of prepared films

1



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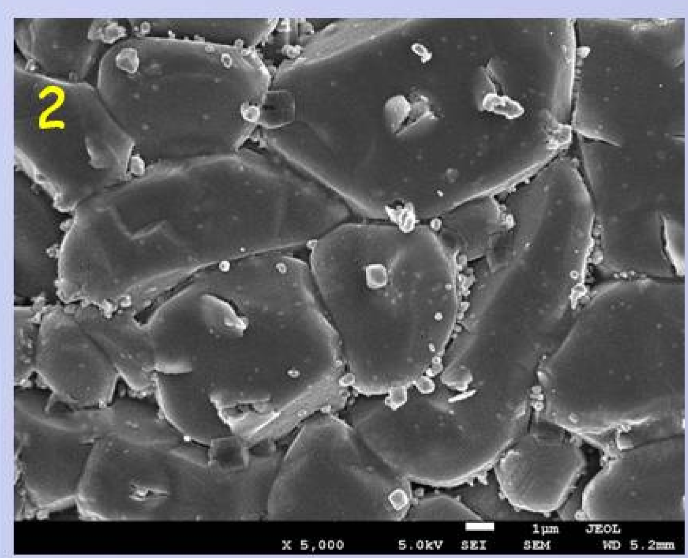

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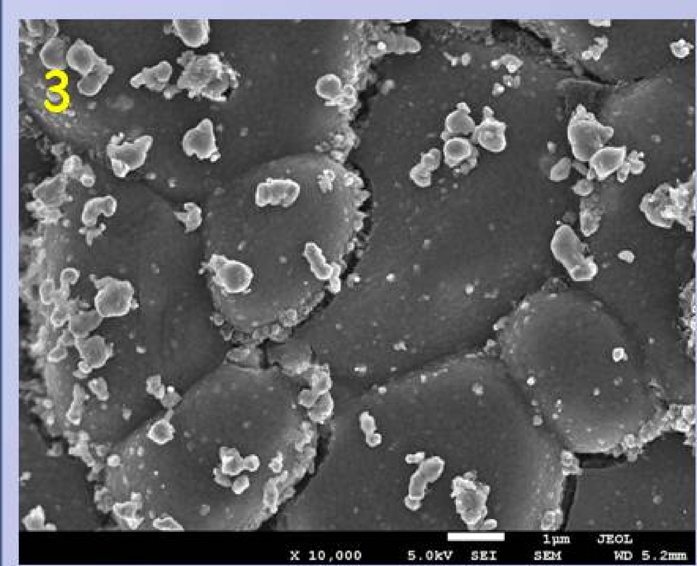

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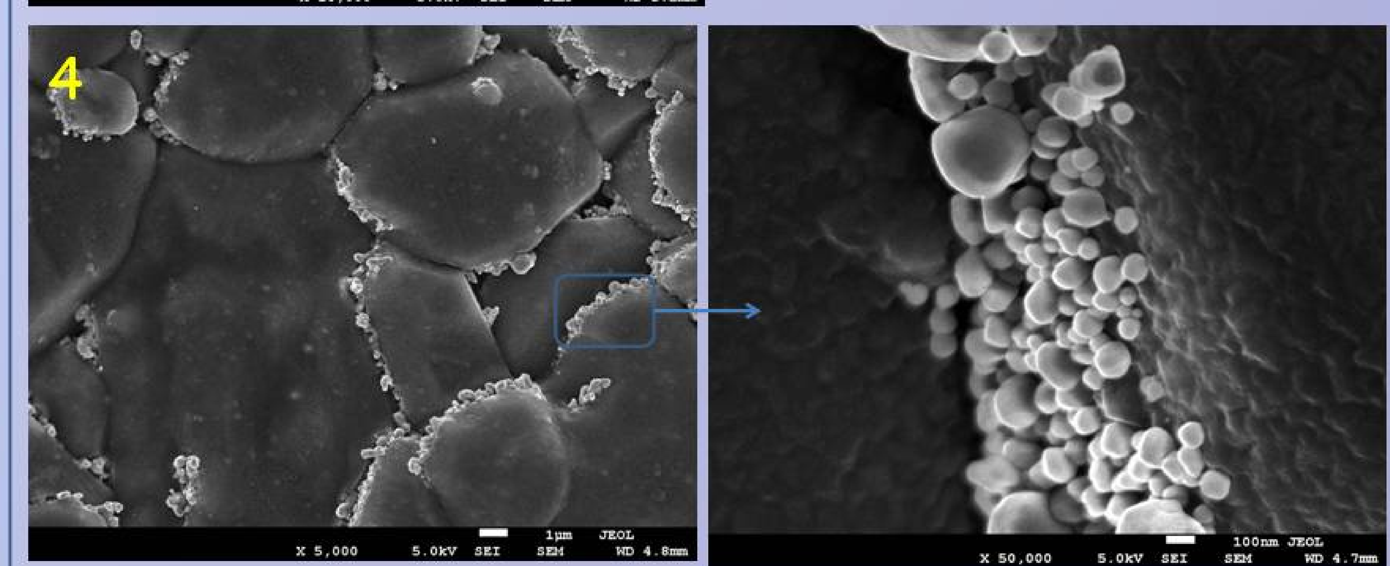

Sample no.	IC60 [A]	I Pd [A]	T [sec]	D [mm]	Xylene dose [ml]	Xylene flow ratio	Time [min]
1	2	1.2	10	54	0,5	0.1 ml/min	5
2	2,1	1,2	8	69	3	0.1 ml/min	30 and 1 hour after CVD process
3	2,1	1,2	10	69	0	0	30
4	1,9	1,3	10	54	3	0.1 ml/min	30 at T=500 °C

Types of film on alundum:

1) Pd nanograins placed in porous carbon matrix
2) Pd nanograins placed in amorphous and nano-carbon matrix
3) Pd nanograins deposited in all volume and on a surface of big areas of alumina grain
4) Pd nanograins are place an edge of big alumina grains

Conclusions:

- Manipulating PVD deposition and modification parameters of CVD process we are able to obtain many type of films reacting in different way on the hydrogen present in ambient atmosphere.
- Types of film are connected to their electric properties (resistance)
- Types of films are connected to the sensitivity of these films toward hydrogen.

References:

1. F.A. Lewis, The Palladium Hydrogen System, Academic Press, London, 1967, p. 50.
2. F. Favier, E.C. Walter, M.P. Zach, T. Benter, R.M. Penner, Science 293 (2001) 2227-2231.

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