FTIR studies of nanostructural C-Pd films for hydrogen sensor applications

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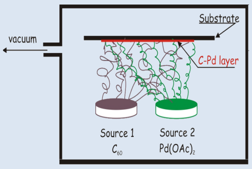
Introduction

Nanocomposite C-Pd films with porous structure and palladium nanograins placed in a carbon matrix are promising materials for hydrogen sensor applications. It is connected with films' high surface area and highly selective hydrogen adsorption/desorption properties of palladium nanocrystals.

Synthesis of the C-Pd films

Nanocomposite C-Pd films were obtained in Physical Vapour Deposition (PVD) process under dynamic vacuum of 1 mPa on various substrates. Fullerene C_{60} and palladium acetate ($Pd(OAc)_2$), evaporated from two separated sources, were used as precursors of carbon and palladium in this process. Films composed of palladium nanograins with the size of 5-10 nm and carbonaceous matrix were obtained in this way.
6 substrate pieces (alumina and quartz) were placed on different positions in relation to sources.



The studies of molecular structure of C-Pd films

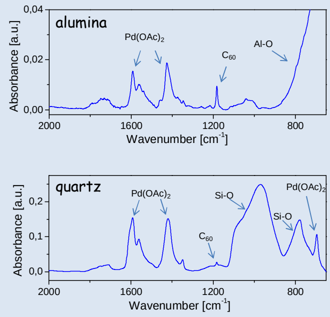


Fig 1. FTIR spectra of C-Pd films deposited on different substrates

- Bands connected with a presence of palladium acetate (C=O symmetric and asymmetric stretching, CH_3 bending vibration) and fullerene (C_{60} pentagon asymmetric deformation) are found in FTIR spectra of C-Pd films . So we deduced that precorsors of these films have not decomposed completely during synthesis process.
- Bands originating from substrates are also visible in these spectra: two bands regarding to symmetric and asymmetric stretching vibrations of Si-O (on quartz substrate) and the absorption band of Al-O bond stretching at the end of the spectral range (for alumina substrate).

The influence of the position of the substrate on the structure of C-Pd films

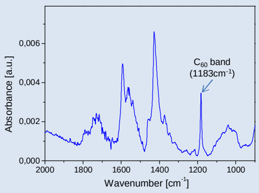


Fig 2. FTIR spectrum of C-Pd film

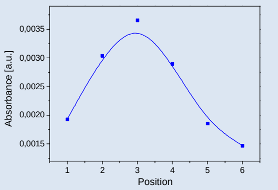


Fig 3. Intensity of the C_{60} band (1183cm^{-1}) as a function of substrate position

- Analysis of FTIR spectra regarding C_{60} band (1183cm^{-1}) enables to study the influence of the substrate position in PVD process on the film's thickness.
- In the central positions (positions 2, 3 and 4), placed nearer the C_{60} source, the highest amount of fullerene is deposited. It means that the thickness of C-Pd films deposited on the central substrates is the highest.
- It is confirmed by the results obtained from UV-Vis spectroscopy (while analysing intensity of C_{60} band - 345nm)
- Closer location of the substrate to the source causes higher thickness of the C-Pd film.

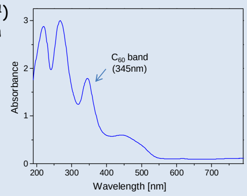


Fig 4. UV-Vis spectrum of C-Pd film

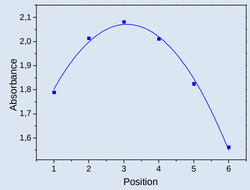


Fig 5. Intensity of the C_{60} band (345nm) as a function of substrate position

The influence of parameters of PVD process on the structure of C-Pd films

Table 1. Parameters of PVD process

Sample	Distance [mm]	I_{Pd} [A]	I_{C60} [A]	t [min]
1C-Pd	54	2,1	1,2	8
2C-Pd	60	2,1	1,2	8
3C-Pd	69	2,1	1,2	8

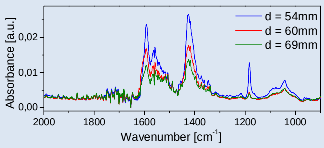


Fig 6. FTIR spectra of C-Pd films obtained at different conditions

The FTIR spectra of samples obtained in PVD process with different distance between sources and substrates show that the intensity of bands regarding to palladium acetate and fullerene decreases with the distance. Decrease of intensity of C_{60} band (1183cm^{-1}) is stronger than decrease of $Pd(OAc)_2$ bands. It can be caused by the increase of the decomposition degree of both compounds. On the other hand decrease of films' thickness also causes decrease of all bands intensity.

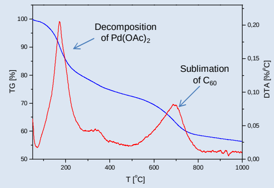


Fig 7. Thermogravimetry analysis of sample 2C-Pd in argon atmosphere

Table 2. Results of TG analysis

Sample	Distance [mm]	$Pd(OAc)_2$ [%]	C_{60} [%]
1C-Pd	54	11,1	34,1
2C-Pd	60	19,9	14,8
3C-Pd	69	18,6	5,1

The results of thermogravimetry analysis confirm that the content of fullerene in C-Pd film decreases with the increase of distance between sources and substrates. It is propably connected with higher molecular mass of fullerene (720u) compared with palladium acetate (224u).

Application of C-Pd films as hydrogen sensors

Table 3. Resistance of the C-Pd films

Sample	Resistance
4C-Pd	*not conducting*
5C-Pd	21,8kΩ

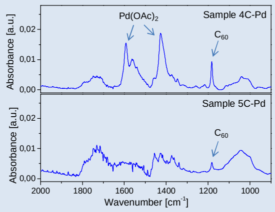


Fig 8. FTIR spectra of C-Pd films obtained in different conditions

Differences in conductivity of C-Pd films synthesized in different conditions can be explained applying FTIR spectra analysis. In spectrum of sample 4C-Pd acetate characteristic bands are found whereas in sample 5C-Pd these bands are not observed. So, we can conclude that palladium acetate in sample 5C-Pd had to be decomposed to Pd nanocrystallites. These metallic grains cause the increase in conductance of this sample.

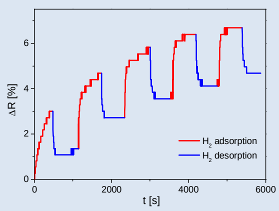


Fig 9. Changes of resistance of C-Pd film in the hydrogen atmosphere

Sample 5C-Pd can be applied as active layer in H_2 sensor because it is sensitive toward hydrogen presence. Hydrogen atmosphere causes the increase of C-Pd film's resistance whereas in absence of H_2 it decreases (Fig. 9). The increase of the resistance is connected to a formation of PdH_x which conductance is lower than metallic Pd. The decrease of the film's resistance is caused by the decomposition of PdH_x during H_2 desorption.

Conclusions:

- FTIR spectroscopy is powerful technique in quality measurements of nanocomposite C-Pd films to determine their composition and molecular structure
- FTIR spectroscopy enables to study the influence of technological parameters of PVD synthesis process on C-Pd films' molecular structure deposited on different substrates
- FTIR spectra of nanocomposite C-Pd films show which films can be applied as hydrogen sensors

This project is co-financed by the European Regional Development Fund within the Innovative Economy Operational Programme 2007-2013 No UDA-POIG.01.03.01-14-071/08-06.

The authors acknowledge that This FINELUMEN International Summer School 2011, Łochów, Poland, was supported by the Project FP7 Marie Curie Initial Training Network, Contract PITN-GA-2008-215399 „Cavity-confined Luminophores for Advanced Photonic Materials: A Training Action for Young Researchers".