Structure of C-Pd thin films

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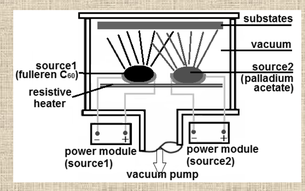
INTRODUCTION

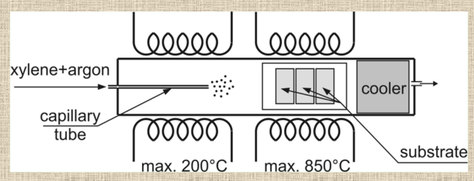
Nanocomposite C-Pd films are promising materials for optoelectronics due to their unique electrical and optical properties [1,2]. The knowledge about the structure, topography and morphology of such films is necessary for further applications [3]. The structure and composition of these films is connected to the structure of nanoobjects forming them. Generally, it could be noticed that films are based on carbonaceous matrix (nanoporous, nanograins of fullerenes or graphite/graphene like nanostructures) in which palladium nanograins are included. Both, size and structure of carbon matrix as well as size and structure of palladium nanograins strongly depend on technological processes parameters. The form of nanoobjects affects on final properties of the film.
Here, we present results of characterization of film composed of nanoporous carbonaceous matrix containing palladium nanograins. These results help us to understand phenomena connected to observed optical properties of films.

EXPERIMENTAL

C-Pd films were obtained by the two steps' PVD/CVD method elaborated in Tele- and Radio Research Institute [4]. In the first step, nanocomposite films formed of carbonaceous matrix with 2-5nm in size palladium nanograins were obtained by PVD (Physical Vapour Deposition) process under a dynamic vacuum of 10^{-5} mbar. As precursors of these films fullerene C_{60} and palladium acetate $Pd(C_2H_3O_2)_2$ were used. These precursors were evaporated from two separated sources [5]. The temperature of substrates in PVD process was 50-70 °C, growing time was 8 minutes and the distance between substrates and sources was 69 mm. For all processes (with applied different substrates) these parameters were the same.

During the second step, nanocomposite films from PVD were modified in CVD process. The pyrolysis of xylene (C_8H_{10}) proceeded in this process. CVD process was performed in a quartz reactor under an argon atmosphere and in the temperature of 650 °C. The total modification time was 30 minutes. The argon flow rate was maintained at 40 l/h while xylene flow rate was 0,1 ml/min. In order to eliminate the xylene residue after stopping of its supply into the quartz reactor, films were annealed in Ar for one hour. In CVD processes all parameters were the same for all used substrates.

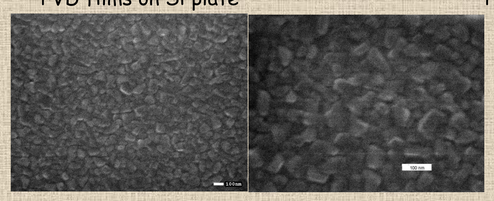




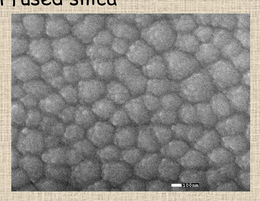
SEM study

The morphology and structure of C-Pd films were studied by Scanning Electron Microscopy (SEM) with JEOL-JSM 7600F microscope with SE (Secondary Electron) detector and with LABE (Low Angle Backscattered Electron) detector showing a contrast composition (carbon and palladium). The microscope was operated at 1keV and 5 keV incident energy.

PVD films on Si plate

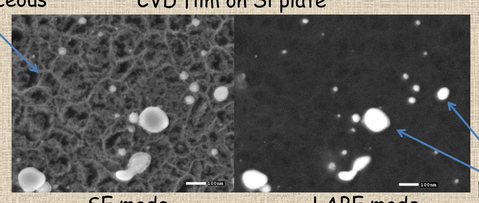


PVD film on fused silica



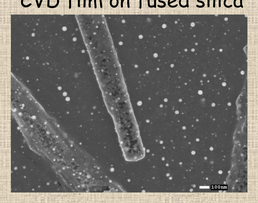
nanoporous carbonaceous matrix

CVD film on Si plate



SE mode LABE mode

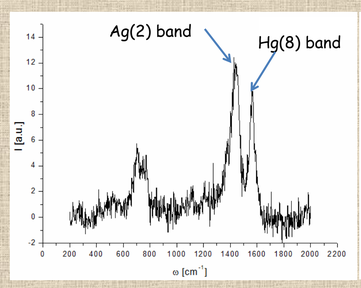
CVD film on fused silica



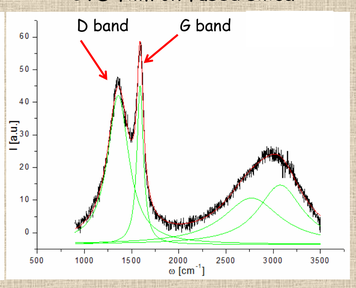
Raman study

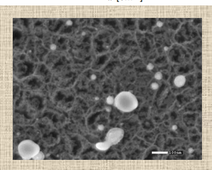
Raman spectra measurements were carried out using Jobin Yvon-Spex T64000 Raman spectrometer with triple-grid monochromator, equipped with confocal microscope and CCD detector (with the resolution of 1024 x 256 pixels) cooled with liquid nitrogen. For the measurements the single monochromatisation was applied, with Rayleigh dispersion used effectively by Notch-type filters. The measurements were carried out in ambient temperature for the excitation wavelength of 514.5 nm.

PVD film on fused silica



CVD film on fused silica





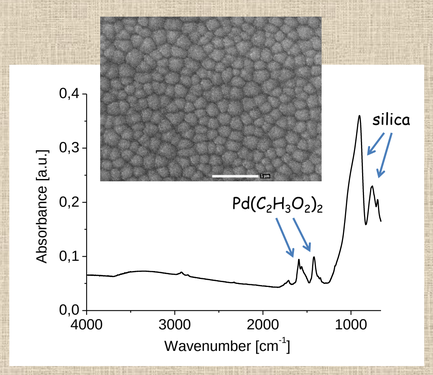
PVD and CVD film

Bands	ω [cm^{-1}]	FWHM
1 (D)	1351	132
2 (G)	1587	40
3 - C60 Ag(2)	1468	66
4 (gases adsorbed from environment)	2771	370
5 (as above)	~3000	290
C60 Ag(2)	~1468	
C60 Hg(8)	~1550	

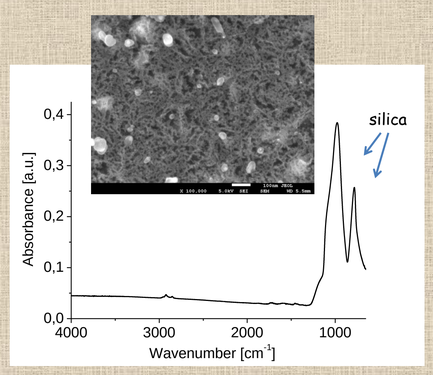
FTIR study

FTIR spectra were obtained with ThermoScientific Nicolet iS10 FTIR spectrometer, using ATR (Attenuated Total Reflectance) technique in the spectral range 650-4000 cm^{-1} at the spectral resolution of 4 cm^{-1}. Spectra were 64 scanned and averaged to reduce the noise.

PVD film on fused silica



CVD film on fused silica



CONCLUSIONS

The influence of parameters of technological processes and substrate's type on structures and properties of C-Pd films obtained in PVD/CVD method was studied. We also found that topography, structure and chemical composition of these films affect on their optical properties. Some observed phenomena cannot be explain on base of collected data and their interpretation and it needs additional studies.

ACKNOWLEDGEMENTS

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REFERENCES

[1] Czerwosz, E., Dłużewski, P., Kęczkowska, J., Kozłowski, M., Suchańska, M. and Wronka,H., "*Palladium nanocrystals and their properties*", Materials Science-Poland 26 (1), 119-125 (2008)
[2] Czerwosz E.] Czerwosz, *"Badania zmian własności przewodnictwa elektrycznego warstw palladowo-węglowych pod wpływem gazów zawierających związki wodoru"*, Przegląd Elektrotechniczny vol. 10, 61-64, 2010.
[3] Kozłowski, M., Diduszko, R., Olszewska, K., Wronka, H. and Czerwosz, E., "Nanostructural palladium films for sensor applications", Vacuum vol. 82, pp.956-961 (2008).
[4] Czerwosz E, Kowalska E, Wronka H, Radomska J, Patent Notification 2008 nr P384 591
[5] E.Czerwosz, R.Diduszko, P.Dłużewski, J.Kęczkowska, M.Kozłowski, J.Rymarczyk, M.Suchańska – *Properties of Pd nanocrystals prepared by PVD method* – Vacuum, vol.82, pp.372-376 (2008),
[6] Guohua Chen , Wengui Weng, Dajun Wu, Cuiling Wu, Jinrong Lu, Pingping Wang, Xiangfeng Chen, *Preparation and characterization of graphite nanosheets from ultrasonic powdering technique,* Carbon vol.42, pp.753–759 (2004)