NANOSTRUCTURAL C-Pd FILMS OBTAINED IN 2-STEPS PVD/CVD TECHNOLOGICAL PROCESS

Mirosław Kozłowski[1], Elżbieta Czerwosz[1], Piotr Dłużewski[2], Ewa Kowalska[1], Joanna Radomska[1], Halina Wronka[1]

[1]Tele & Radio Research Institute, Ratuszowa 11, 03-450 Warsaw
[2]Institute of Physics PAS, Aleja Lotników 32/46, Warsaw

Abstract
Results of electron microscopy methods studies of nanoporous films composed of carbon and palladium (C-Pd films) and obtained in 2-steps method (PVD/CVD) are presented. The influence of different technological parameters on the structure of these films was studied. TEM and SEM studies show that a structure of Pd is of fcc type and structure carbonaceous nanoobjects is graphene-like. Topography and morphology of films obtained in both technological steps were also investigated.

Tab. 1. Description used for studied samples

Pd content [wt. %]	Sample obtained in technological step	
	PVD	PVD/CVD
8	PVD1	CVD1
26	PVD2	CVD2

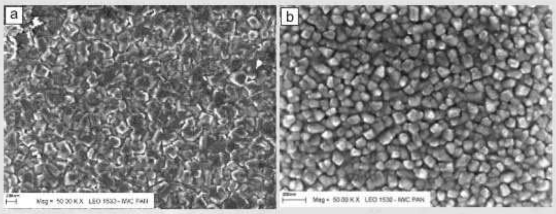
Fig.2. Typical SEM image of Pd-C film after PVD process for a) PVD1, b) PVD2 samples


Fig.1a. PVD set-up

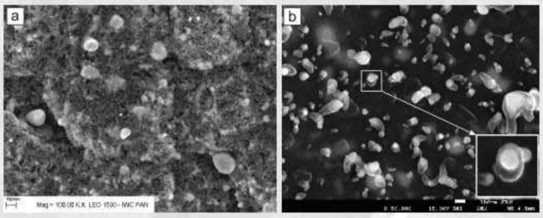
Fig.3 SEM images for CVD1 (a) and CVD2 (b) samples

Topography of CVD1 and CVD2 films modified by CVD process with temperature 650°C are shown in Fig.3. For film with lower Pd content higher porosity of carbonaceous matrix was observed while the size of palladium nanocrystals is higher. On the other hand for higher Pd content observed palladium nanocrystals are enveloped with carbon what is clearly visible in Fig.3b. In inset in Fig.3b such nanoobject is presented. This nanoobject has bright core and darker shell.

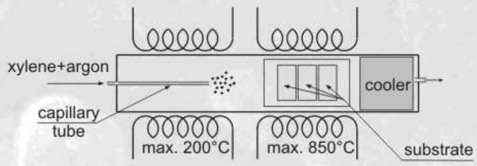

Fig.1b. Schema of experimental CVD set-up

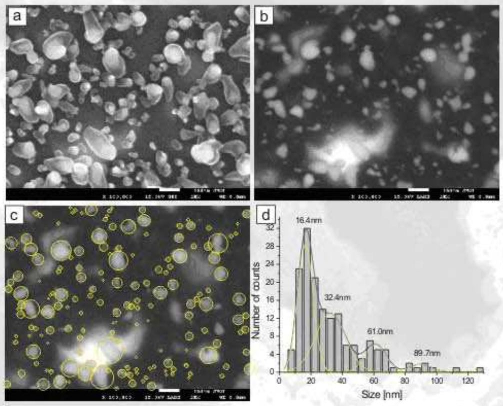

Fig.4 SEM images of CVD2 sample: a) SEI mode; b) BEI mode, c) size analysis - circles circumscribed on nanocrystals represents its diameter, d) histogram of nanocrystals size

SEM study of CVD1 film modified at different temperatures shows that the optimal temperature for obtaining film of nanoporous structures with a highly developed specific surface area is 650°C. At this temperature a formation of the carbon nanoporous film like sponge material containing Pd nanograins was observed. This porous carbonaceous skeleton exhibits large specific surface area with open cell structures.
Temperature of 550°C is too low for synthesis of porous material. In this temperature PVD1 film is only cracked (Fig.7a) and grains characteristic for PVD films are still observed. It is probably that at this temperature Pd nanoparticles present too low mobility and they do not agglomerate into larger particles. This temperature is also to low to cause catalytic reaction and formation of enveloped Pd nanocrystals.
The modification at temperatures of 700°C and 750°C seem to be too high for forming nanoporous structures (Fig.7c,d) but they lead to a growth of bigger C-Pd crystalline forms. In temperature range 700 ÷ 750 °C boundaries between the clusters of grains are still visible.

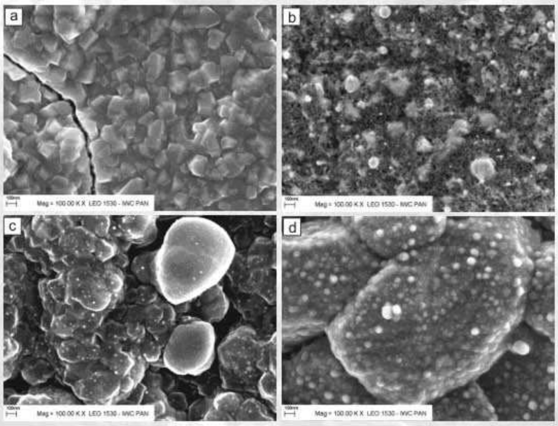
Fig.7. SEM images of CVD1 films modified at different temperatures a) 550°C, b) 650°C, c) 700°C, d) 750°C

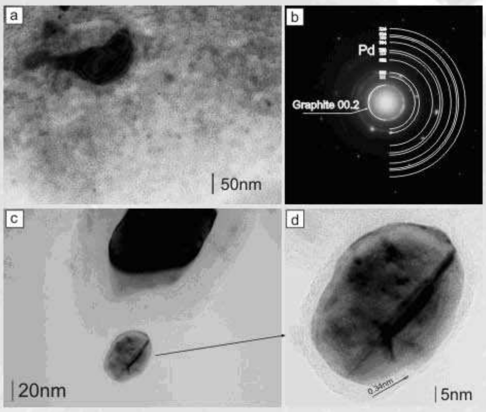

Fig.5. TEM investigations of CVD1 sample, a) film's structure, b) diffraction pattern c, d) Pd nanocrystals with visible

In Fig.5 and in Fig.6 results of TEM studies for CVD1 and CVD2 samples respectively are presented. For lower palladium content the size of Pd nanocrystals is lower than size of objects found in films with higher Pd content. Beside of this the amount of palladium objects observed in CVD1 film is much lower than the amount of such object observed for CVD2 films. In both cases palladium is enveloped in carbon shells (fig.5c. and Fig.6c). Palladium core has fcc type of structure for both kinds of films. In diffraction images we observe rings originating from crystallographic planes of Pd (Fig.5b and Fig.6b). The strongest ring origins from 00.2 planes of graphite. In TEM images (Fig.5c,d and Fig.6c,d) planes of graphite are visible and they form a multi-shell structure in which Pd single crystals is placed. This shell protects Pd core from the influence of various chemical agents (e.g. oxygen). Additionally graphite grains may be formed in a C-Pd film as a result of conversion of residue C_{60} under the influence of temperature in the CVD process, as well as the distribution of xylene

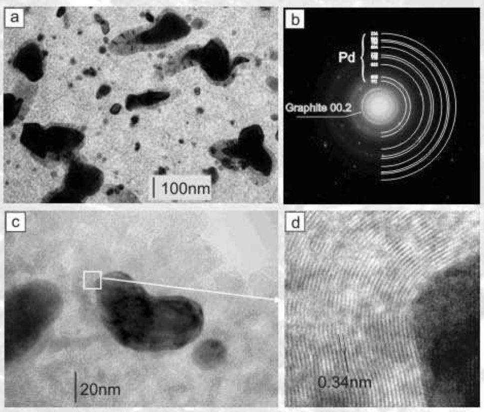

Fig.6 TEM investigations of CVD2 sample, a) film's structure, b) diffraction pattern, c, d) Pd nanocrystals with visible

Conclusions
Investigated nanoporous layers containing carbon and palladium have been obtained in different thermodynamic conditions and on different substrates. Our studies have shown that the degree of development of their areas (nanoporosity) strongly depend on the CVD process condition, especially temperature. Films obtained in PVD process contain various number of Pd nanocrystals with various sizes

Acknowlegment
This research was co-financed by the European Regional Development Fund within the Innovative Economy Operational Programme 2007-2013 (No UDA-POIG.01.03.01-14-071/08-00).