Properties of Pd-C films for hydrogen store applications

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Tab.1. Technological parameters of PVD processes

Sample	Intensity of evaporation		Time [min.]	Substrate
	I_{C60} [A]	I_M [A]		
S1-167	2	1,2	10	Al_2O_3 / Mo
S2-170	2,1	1,2	10	Al_2O_3 / Mo / Si
S3-163	2,1	1,2	8	Si

Carbon nanoporous films (Pd-C films) containing Pd nanograins are a subject of many studies because of a possibility of their applications in hydrogen storage devices and hydrogen sensors of different type. Development of a carbon surface and size of Pd nanocrystals, size and volume of pores affect on the amount of hydrogen adsorbed and absorbed by these films. Nanoporous Pd-C films were prepared by a two-step method consisted of physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes. In PVD process, a nanocomposite film composed of Pd nanocrystals embedded in a carbonaceous matrix was obtained and in the second step this film was modified in CVD process by xylene pyrolysis at the temperature of 650°C. PVD films were evaporated from two separated sources containing fullerene C_{60} and palladium acetate.

AFM results after PVD process

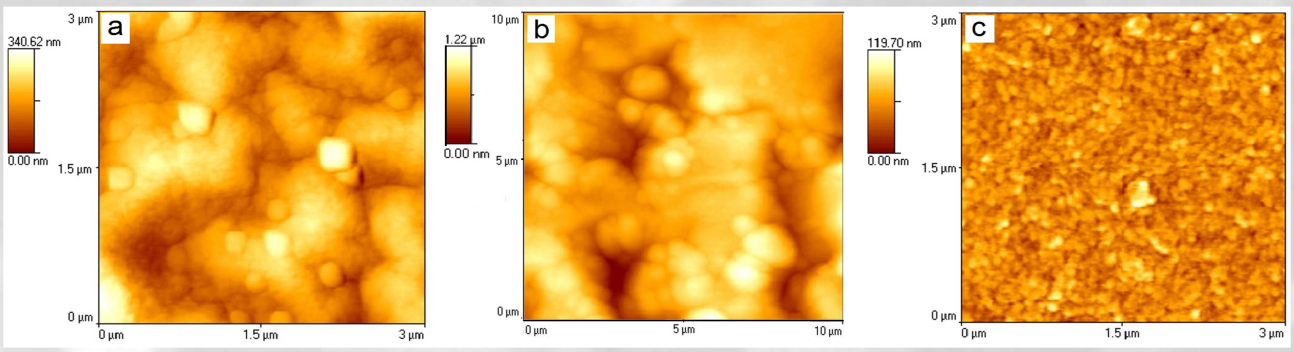

Fig.1. AFM images of Pd-C films after PVD process a) S1-PVD / Mo; b) S2-PVD / Al_2O_3; c) S3-PVD / Si

Tab.2. Surface analysis

	Average roughness [nm]
S1-PVD / Mo	38.5
S2-PVD / Mo	12.5
S3-PVD / Si	9.7

TEM results after PVD process

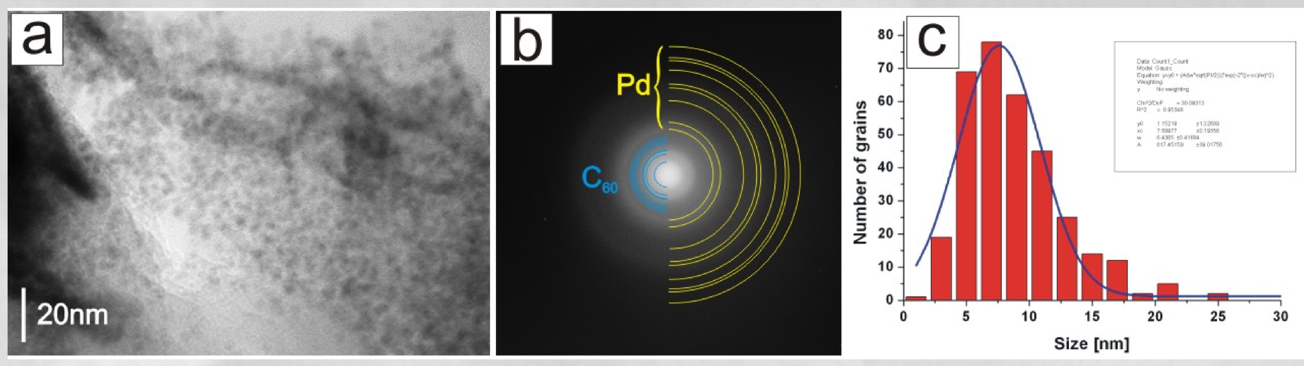

Fig.3. TEM image of S1-PVD sample a) film's structure; b) electron diffraction pattern; c) histogram of Pd nanograins size distribution

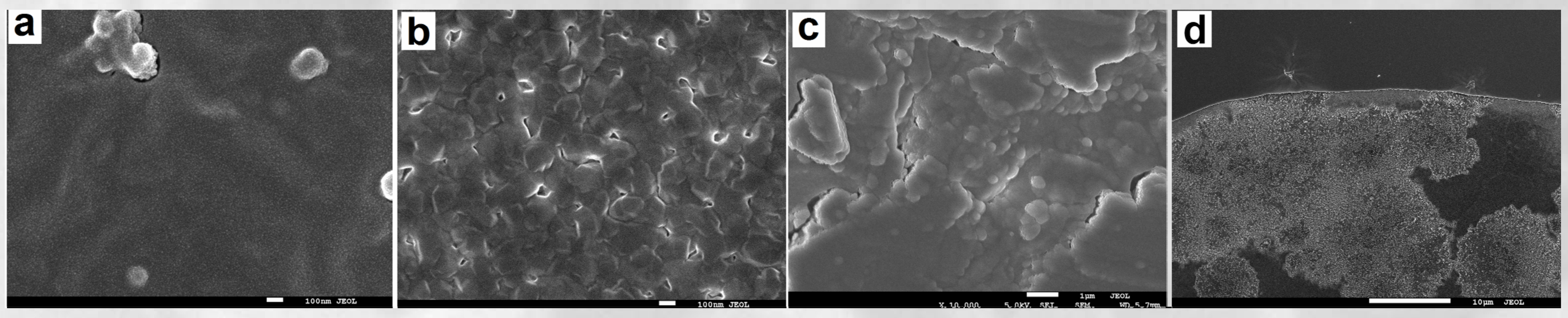

Fig.2. SEM image of Pd-C films after PVD process a) S1-PVD / Mo; b) S2-PVD / Mo; c) S2-PVD / Al_2O_3; d) S3-PVD / Si

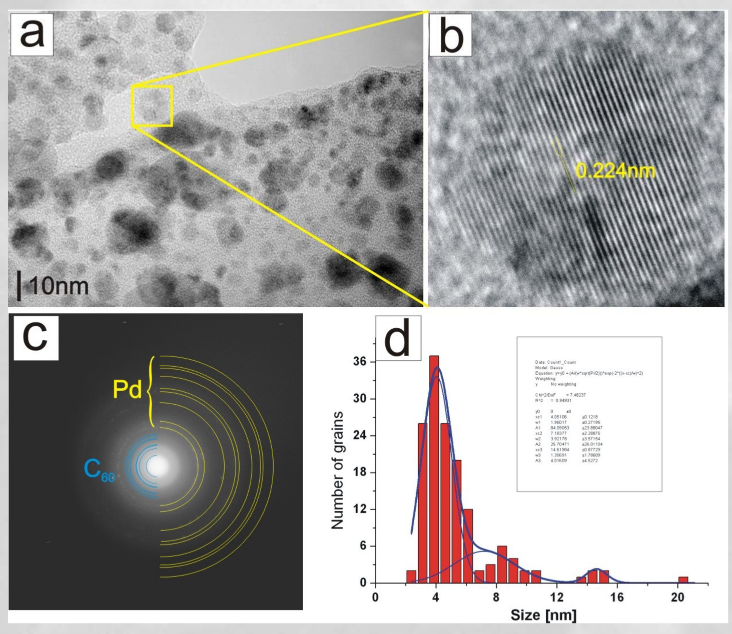

Fig.4. TEM image of S2-PVD sample a) film's structure; b) high resolution image from Pd crystallite with (*fcc*) cubic structure; c) electron diffraction pattern; d) histogram of Pd nanograins size distribution

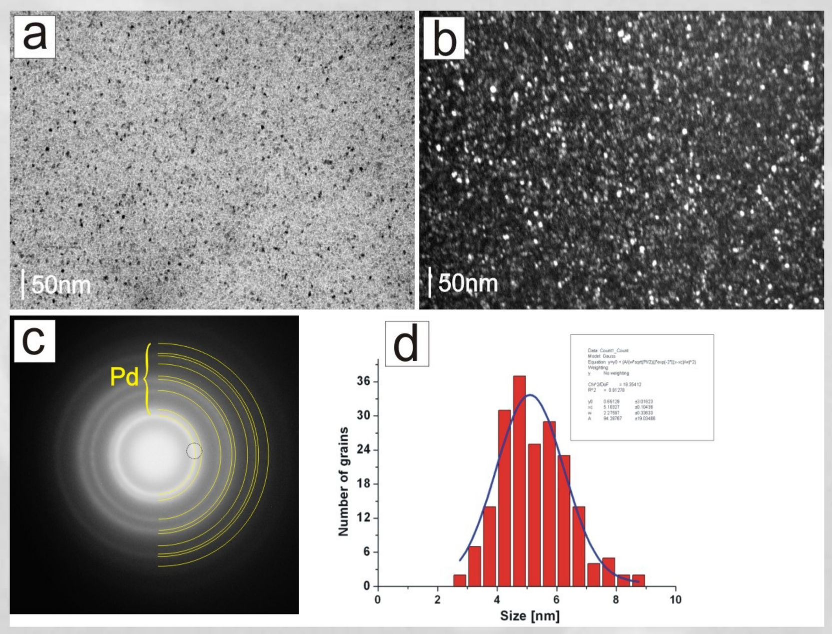

Fig.5. TEM image of S3-PVD sample a) film's structure; b) dark field mode in this area; c) electron diffraction pattern; d) histogram of Pd nanograins size distribution

The parameters of PVD process (sources temperature, process duration time) affect on the final form of PVD samples. AFM and SEM studies show different topography of sample S1-PVD and sample S2-PVD obtained with different technological parameters. Sample S1-PVD which was evaporated on the same substrate (Mo) but with lower temperature of C_{60} evaporation than sample S2-PVD has higher average roughness.

Substrate type affects on the structure of PVD films. Films deposited on different substrates (with various flatness) in the same technological parameters have different topography and structure (sample S2-PVD). Sample evaporated on Si has poor adhesion and two-layer structure.

Films obtained in the PVD process are built of Pd nanograins (*fcc* type) embedded in a carbon matrix composed of a mixture of fullerene, graphite and amorphous carbon phases. TEM investigation proves it.

TEM results after CVD process

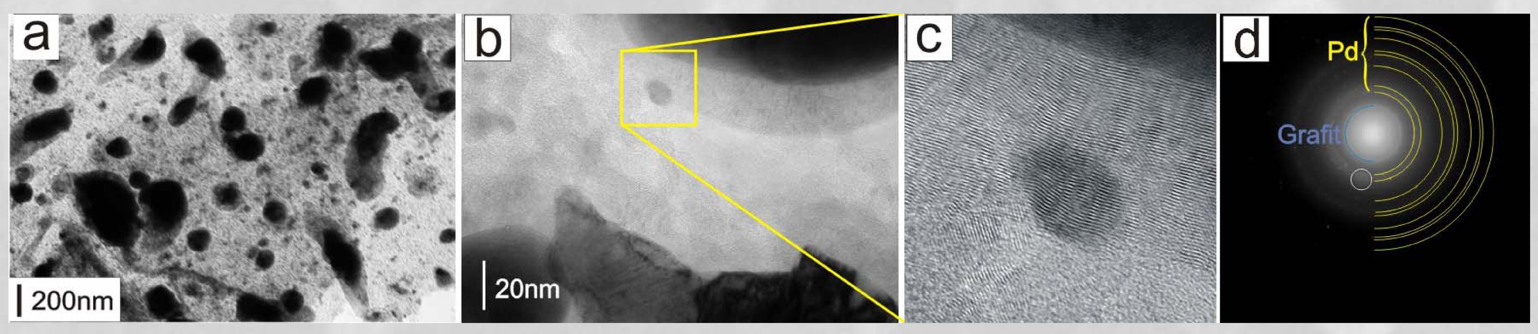

Fig.7. TEM image of S1-CVD sample a) film's structure; b) Pd nanocrystals with visible graphite multi-shell; c) high resolution image from graphite multi-shell; d) electron diffraction pattern

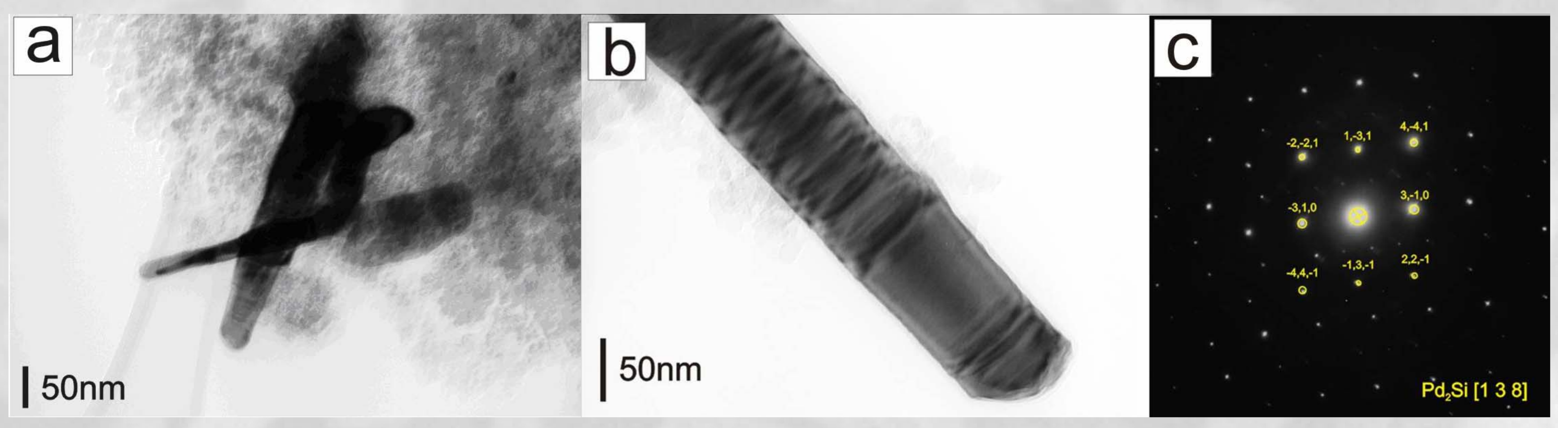

Fig.8. a, b) TEM image of Pd_2Si nanoneedle; b) electron diffraction pattern

SEM results after CVD process

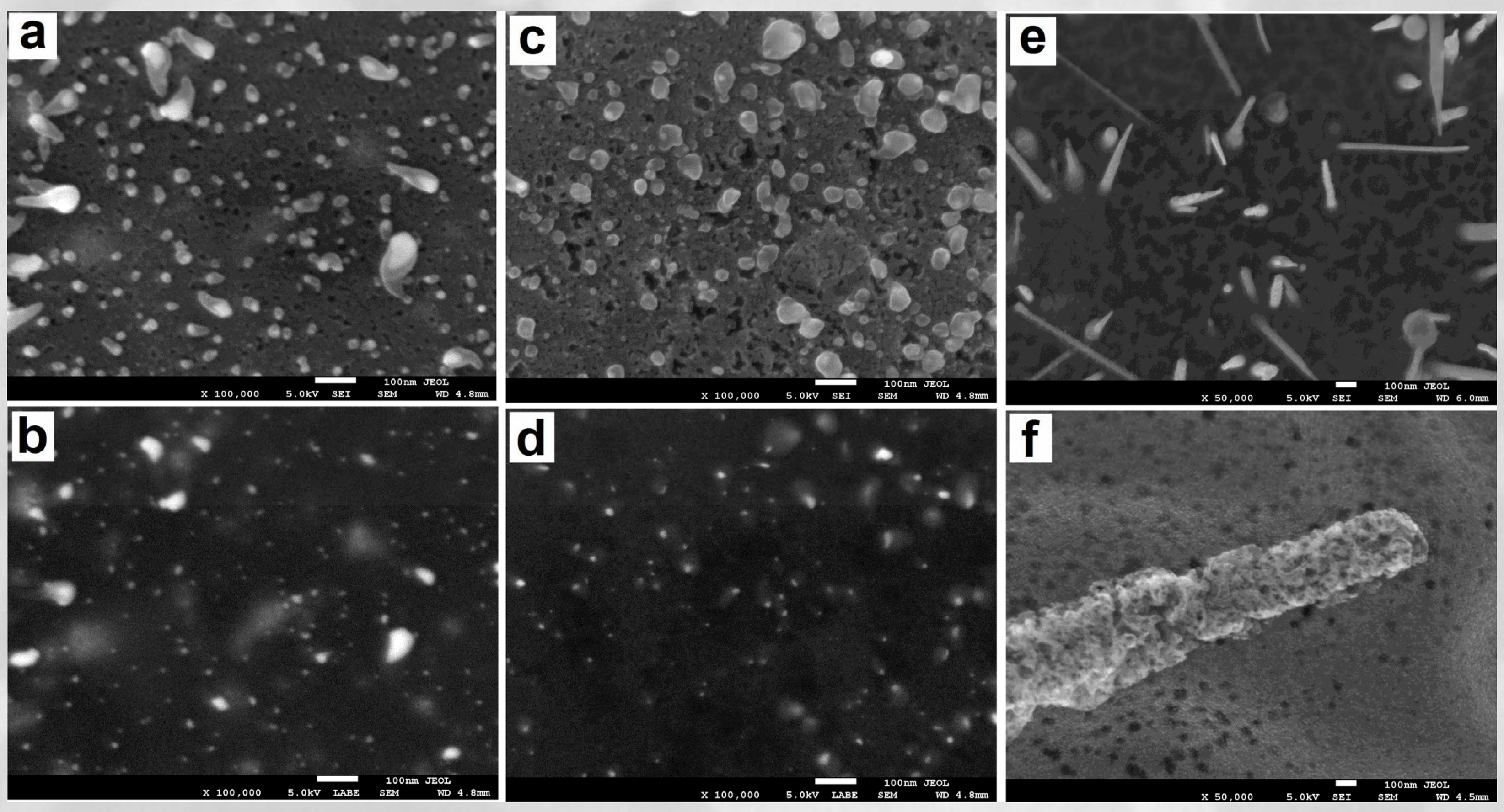

Fig.6. SEM image of Pd-C films after II process a) S1-CVD SEI mode b) S1-CVD BEI mode, c) S2-CVD SEI mode, d) S2-CVD BEI mode, e) surface S3-CVD sample, f) SEI mode interior of S3-CVD, g) BEI mode interior of S3-CVD

The form and structure of PVD films cause various growth of CVD film with different structure. SEM and TEM results show that all samples obtained in CVD modification become less uniform in respect of palladium grains size while depositing on Mo or Al_2O_3 substrate. The catalytic reaction of palladium with silicon causes the growth of Pd_2Si nanocrystals in form of nanoneedles.

The influence of parameters of CVD process such as temperature and xylene amount causes an arise of porous carbonaceous matrix in which palladium nanoparticles surrounded by graphite shells are placed. These graphite shells creation could be connected to process of C_{60} degradation (fullerite nanocrystals present in PVD samples) due to high temperature and palladium interaction.

Under the influence of the CVD process temperature metal nanograins could migrate and agglomerate into bigger clusters.

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