

Morphological, topographical and FTIR characterizations of Pd–C films

JOANNA RYMARCZYK¹, ANNA KAMIŃSKA¹, JUSTYNA KĘCZKOWSKA²,
MIROSLAW KOZŁOWSKI¹, ELŻBIETA CZERWOSZ^{1*}

¹Tele & Radio Research Institute, Ratuszowa 11, 03-450 Warsaw, Poland

²Kielce University of Technology, al. 1000-lecia PP 7, 25-413 Kielce, Poland

*Corresponding author: elzbieta.czerwosz@itr.org.pl

The structure, topography and morphology of Pd–C films were studied by AFM (atomic force microscopy), SEM (scanning electron microscopy), Raman and FTIR (Fourier transform infrared spectroscopy) methods. It was found that an increasing content of palladium in films causes a decrease in their roughness and size of nanograins. The topography and morphology of Pd–C films depend on the content of palladium in the film, what was found from the analysis of SEM and AFM images. FTIR and Raman spectra show that the content of fullerene and palladium in the film strongly depends on technological parameters of PVD (physical vapor deposition) process.

Keywords: palladium nanocrystals, fullerene, PVD.

1. Introduction

The reactions of transition metal complexes with fullerenes result in the formation of an interesting array of new compounds. Some reactions lead to the formation of new complexes by an addition of ligating groups to the fullerene so that the metal center is attached to the fullerene through some type of a bridging arrangement [1]. It was also found that C₆₀ with some compounds and transition metals form polymers. For example, the existence of C₆₀Pd_n was proposed [2]. Polymeric materials with higher Pd/C₆₀ ratios are believed to have palladium atoms that cross-link two chains. Heating solid C₆₀Pd₁ in toluene results in the partial dissolution of C₆₀ and the formation of a solid with a Pd/C₆₀ ratio between 2 and 3. These polymers have also been examined by electron microscopy [3]. For C₆₀Pd₃, one-fourth of the sample consisted of small crystals of Pd in an amorphous matrix. The rest of the sample was free of Pd crystals and showed local crystallinity. Ten percent of the material gave an electron diffraction pattern that was interpreted in terms of a model of a C₆₀Pd₆ octahedral unit with each palladium center bridging two fullerene units. For studying of structural properties of

such materials usually XRD, Raman and FTIR methods are used. When obtained crystals are smaller than 100 nm in size, XRD cannot be applied. The Raman spectroscopy is better tool for studying of small size and low-ordered objects. For example, the Raman spectra of palladium compounds show clear evidence of the lower symmetry of C_{60} when it is bound to a metal atom [4]. While C_{60} itself has only 10 vibrations (of the possible 174 modes) that are Raman-active, the adducts show additional Raman-active, fullerene-derived bands. Other methods as SEM and AFM are very useful for topographical and morphological investigations. From AFM studies, a roughness $R_{sa} = A_{3D}/A_{2D}$ of polymer C_{60} -Pd was measured and it was determined as 1.37 [5].

In this paper we present the results of study of Pd-C films obtained by physical vapor deposition (PVD) method where precursors are fullerene C_{60} and palladium acetate. Depending on technological parameters, we are able to obtain a fullerene-palladium composite film, composite palladium acetate reach film with palladium and amorphous carbon nanograins as well as a polymer C_{60} -Pd film. From our previous TEM and selected area electron diffraction (SAED) investigations of Pd-C films with various Pd content [6] we know that all films contain Pd *fcc* type of nanocrystals embedded in a matrix composed of a form of carbon (fullerite grains, amorphous carbon grains, loosely connected graphite planes) depending on the preparation mode and Pd content. It was also found that the size of Pd nanocrystals depends on Pd content in the film and it is the biggest (8–10 nm) for the film with the lowest Pd content. Here we discuss the influence of these matrixes forms on the morphology and topography of these films.

2. Experiment

Nanostructural carbonaceous films containing nanograins of palladium were prepared by PVD method. The evaporation of fullerene C_{60} and palladium acetate in the PVD chamber was carried out from two separated sources under dynamic vacuum of 2×10^{-6} mbar. In Table 1 the parameters of PVD process are presented.

Pd content changes from sample to sample depending on technological parameters. We present the results of AFM studies of roughness, FTIR studies of molecular structure changes in the film with different Pd content and SEM with EDS microanalysis studies of morphology of Pd-C films. AFM and SEM results showed the topography of films.

T a b l e 1. Technological parameters of PVD processes.

Sample	Intensity of current through a source (C_{60} and Pd)		Time [min]
	I_{C60} [A]	I_{Pd} [A]	
S1	2	1.2	10
S2	2	1.1	10
S3	2	1.0	10

AFM experiment was performed with AFM-EXPLORER 2000 microscope with a standard Si_3N_4 cantilever model MLCT-EXMT-A in a contact mode. FTIR measurements were performed with ThermoScientific Nicolet iS10 FTIR spectrometer, using ATR (attenuated total reflectance) technique in the spectral range $650\text{--}4000\text{ cm}^{-1}$ at the spectral resolution of 4 cm^{-1} . SEM and EDS microanalyses were done with field emission scanning electron microscope (SEM) JEOL-JSM 7600F operating at 5 keV incident energy. Typical secondary electron image (SEI mode) was used to study the surface topography of samples.

EDS measurements were performed with INCA ENERGY 250. In a quantitative analysis CaCO_3 and pure Pd were used as standards of C and Pd, respectively. The found result was an average of 10 points.

3. Results and discussion

3.1. SEM and EDS results

SEM images of all samples obtained by PVD method are shown in Fig. 1. These films have different topography. SEM image of S1 sample (Fig. 1a) shows that the film surface is smooth, layers of the film are built of small grains. From the analysis of SEM image we can estimate that a diameter of these nanograins is between 30 and 50 nm. They seem to be very uniform and flat. The topography and morphology of S2 sample (Fig. 1b) is different from S1 sample. The entire surface of the film is coated with tightly grouped nanograins with a diameter of 100–300 nm. The surface of this film is not so smooth as the surface of S2 sample which is visible in better contrast of SEM images. These nanograins are composed of smaller objects but their size does not allow for EDS microanalysis of their composition. For S3 sample (Fig. 1c)

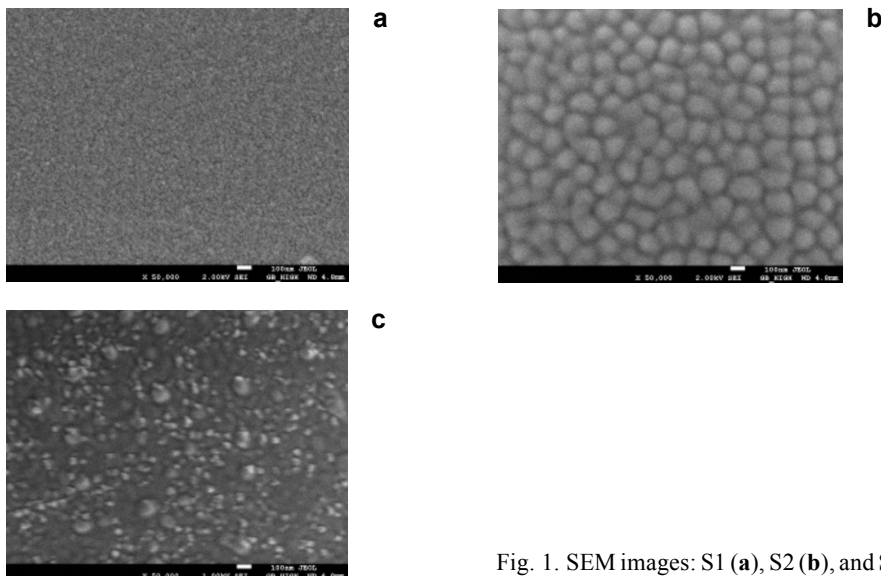


Fig. 1. SEM images: S1 (a), S2 (b), and S3 (c) samples.

T a b l e 2. Pd content from EDS measurements.

Sample	Pd content [wt%]
S1-390	21.12
S2-389	14.16
S3-391	5.12

individual grains on a flat surface of the film are visible. This flat surface could be a film layer that was formed before the individual grains were grown. This sample has poor conductivity which caused poor contrast of SEM image and which is connected to low Pd content. Three kinds of grains are observed and their diameter is between 50–70 nm, ~100 nm and above 150 nm. On the surface, among these grains, the smallest grains with the size of several nanometers could be found.

Energy dispersive spectroscopy (EDS) method was used for a quantitative analysis of Pd–C films. The determined concentration of Pd in Pd–C film is influenced by a substrate composition because of penetration of a substrate by an electron beam in a case when the film thickness is lower than the penetration depth. All measured thicknesses of the studied film were the same and equal to ~300–400 nm. Finally, the weight concentration of Pd was determined as the function of Pd content and the carbon content in the film. In this way, the quantitative analysis of the ratio of Pd/C content in Pd–C films on glass substrate was performed. In Table 2 the result of such analysis is presented.

3.2. AFM result

In Figure 2 the results of AFM measurement for S1, S2 and S3 samples are shown. The roughness of these films is also presented in Table 3.

T a b l e 3. Surface analysis.

	Average roughness [nm]
S1	1.65
S2	5.22
S3	10

AFM results are consistent with the results obtained by SEM. The surface of sample S1 (Fig. 2a) consists of very small grains. The height of nanograins is a few nanometers (4–6 nm). The average roughness for this sample is the lowest and it is 1.65 nm. AFM image of S2 sample (Fig. 2b) shows that the film consists of small grains which cover the entire surface. The average roughness is higher and is 5.22 nm. From the analysis of AFM image we can estimate that a diameter of these nanograins is between 180 and 220 nm and their height is ~30 nm. This topography is similar to the topography of pure C₆₀ films on various substrates, which was studied with AFM earlier [7, 8]. It could suggest that our film has a rather fullerite-like character.

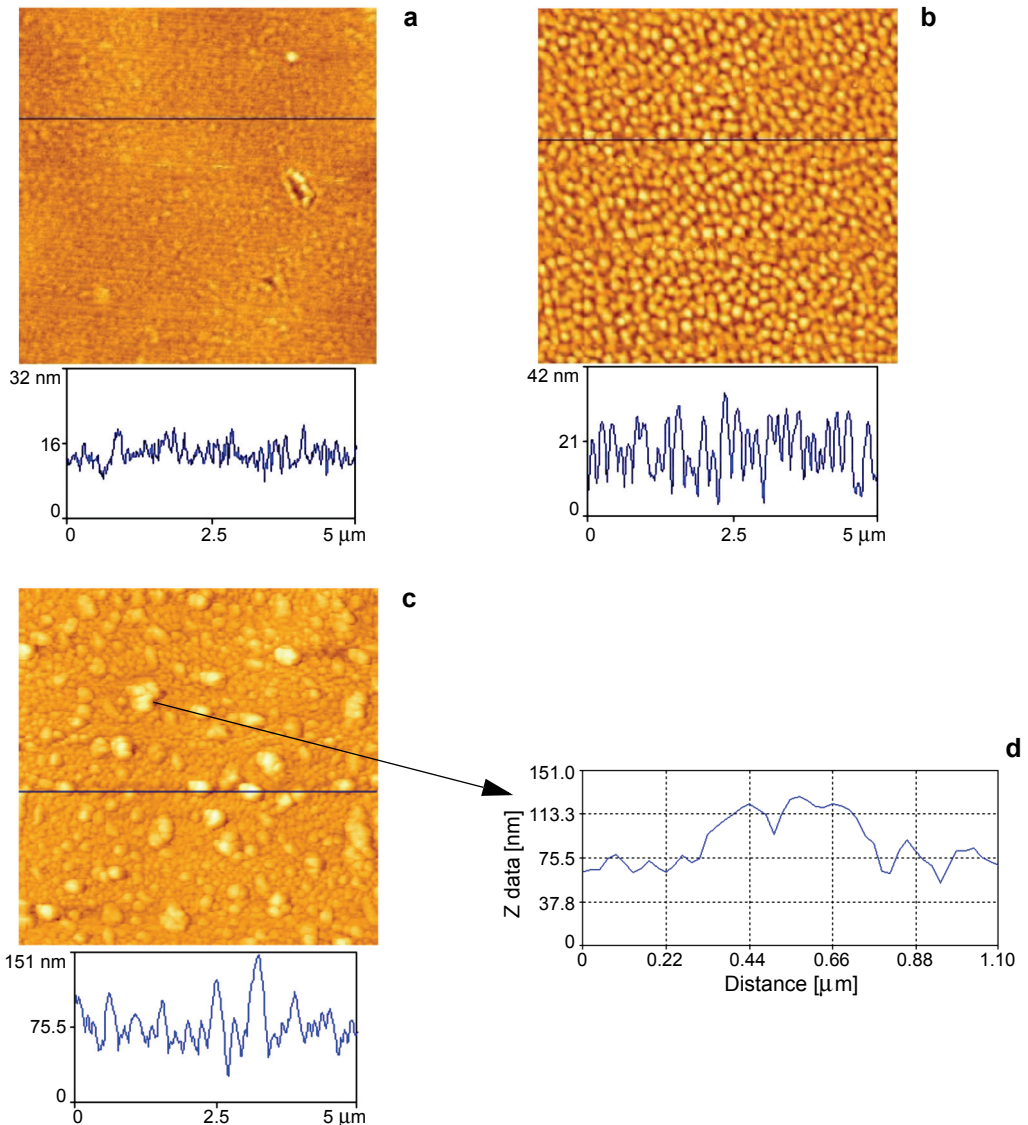


Fig. 2. AFM images with surface analysis S1 (a), S2 (b), and S3 (c) sample ($5 \times 5 \mu\text{m}$); surface analysis of the separated grain (d).

The surface of S3 sample also differs from the previous films. AFM images of this film are shown in Fig. 2c. On this surface, separated grains are visible and the surface between them is covered with very small grains. The height of these separated nanograins is to 80 nm over the surface of the film. In the AFM image, one can see that big grains are built of smaller grains with a diameter of 400 nm (Fig. 2d).

Our results showed that with an increasing content of palladium in films their roughness and the size of nanograins decrease. It was also found that for the highest

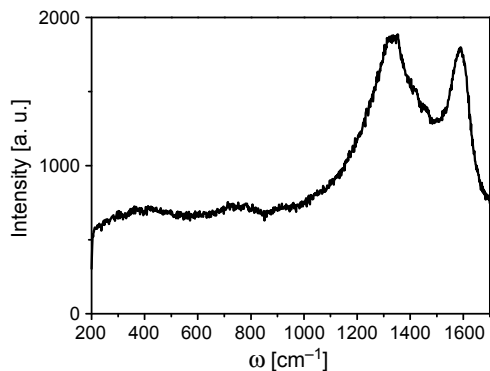
amount of palladium, the size and composition of the grains observed on the film surface is about few nm, while for the lowest palladium content in the film it is uniform and the size of grains varies from 50 nm to ~100 nm.

3.3. Raman and FTIR results

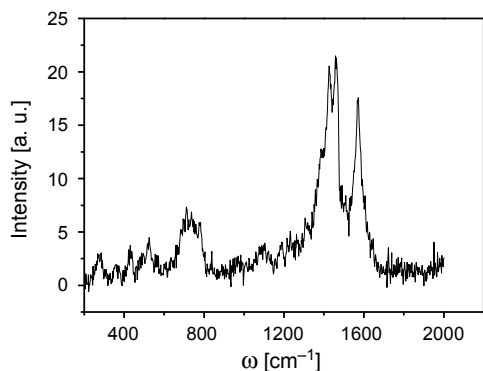
Raman spectrum of sample S1 is shown in Fig. 3. Two bands are dominating in this spectrum. They are placed at 1330 and 1590 cm^{-1} that could be attributed to *D* and *G* bands observed for example in activated charcoal [9]. This means that it is of an amorphous structure.

Raman spectrum of sample S2 is presented in Fig. 4. Some observed bands are attributed to C_{60} molecule vibrations (bands at about 273, 433, 498, 711, 775, 1427, 1469 and 1578 cm^{-1} [10]). In this spectrum we also found the bands that could be connected to vibrations of C_{60} -Pd polymer chains (bands at about 268, 352, 426, 519, 585, 693, 728, 778, 1080, 1371, 1445 and 1564 cm^{-1} [5]). Such spectrum suggests that in our film fullerene grains and polymer C_{60} -Pd grains coexist.

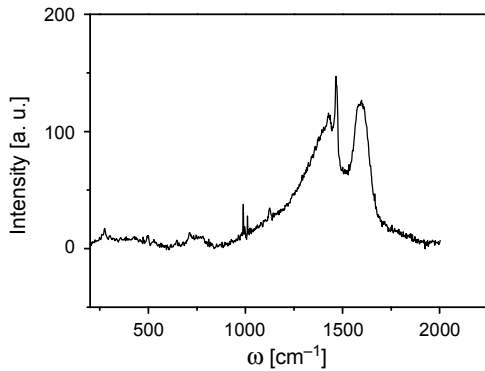
Raman spectrum of sample S3 is presented in Fig. 5. In this spectrum, the bands belonging to C_{60} molecule vibrations as broadbands at about 1320, 1420 and 1590 cm^{-1} are observed. Such bands were found in Raman spectra of high temperature



◀ Fig. 3. Raman spectrum of sample S1.



◀ Fig. 4. Raman spectrum of sample S2.



◀ Fig. 5. Raman spectrum of sample S3.

annealed nanographite films [9]. We can deduce that our film contains fullerene grains as well as nanographite grains.

In Figure 6 FTIR spectra of samples deposited on Mo substrate are presented. For comparison, FTIR spectra of fullerene C_{60} and palladium acetate in KBr pellets are also shown. In the spectrum of C_{60} (Fig. 6d) one can find two narrow bands characteristic of fullerene molecules vibration (the band at 1183 cm^{-1} is attributed to $T_{1u}(3)$ mode and the band at 1428 cm^{-1} is connected with $T_{1u}(4)$ mode [11]). In the palladium acetate spectrum (Fig. 6e), broadbands associated with asymmetric stretching vibrations of C-O bond of carboxylate groups (1605 cm^{-1}), symmetric

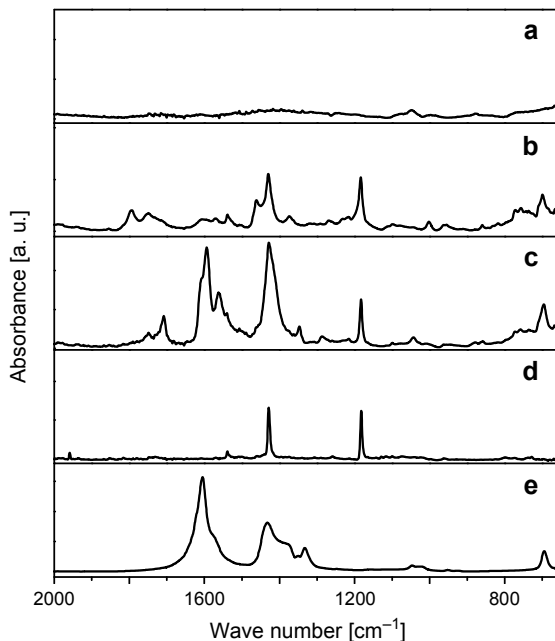


Fig. 6. FTIR spectra sample S1 (a), S2 (b), S3 (c), fullerene (d), and palladium acetate (e).

stretching vibrations of the same C–O bond (1430 cm^{-1}) and CH_3 bending vibrations (1335 and 695 cm^{-1}) are found [12].

In S1 sample spectra (Fig. 6a), the presented absorption spectrum is flat and no bands are observed. In S2 sample spectra (Fig. 6b) we found two bands ascribed to fullerene, while palladium acetate characteristic bands are absent. In the spectrum of S3 sample (Fig. 6c) the bands connected to C_{60} (1183 cm^{-1}) and palladium acetate (1594 , 1427 and 698 cm^{-1}) were found. The second characteristic fullerene band is overlapped with $\text{Pd}(\text{OAc})_2$ band. In sample S2 and S3 spectra we observe the band at a wave number 1750 cm^{-1} , which can be ascribed to the absorption of the ester groups [13]. The band at 1462 cm^{-1} , found in S1 film spectrum, is connected with palladium fulleride vibration [14]. In the region of $780\text{--}660\text{ cm}^{-1}$ (772 , 757 , 744 , 737 , 700 and 660 cm^{-1} for S2 sample; 773 , 759 , 736 and 668 cm^{-1} for S3 sample), the bands characteristic of the metal polymer C_{60}Pd_n are observed [15]. In Figs. 6b and 6c we can also find the bands connected with C–H and C–C vibrational modes [9]: 1606 , 1571 , 1562 and 1539 cm^{-1} (C–C with sp^3 hybridization), 1374 cm^{-1} (C–H with sp^3 hybridization) as well as 1287 and 1269 cm^{-1} (C–H with sp^2/sp^3 hybridization).

FTIR spectra of S2 and S3 samples confirm our conclusion taken from the analysis of Raman spectra for these samples.

Taking into account our previous [6] results from TEM and SAED investigations and the results presented here, we can conclude that the topography of our samples is mainly connected with Pd content and this depends on the technological parameters. For the lowest Pd content we have obtained the film with the highest roughness; grains in the film are of different sizes and they are composed of nanographite, fullerenes grains, palladium acetate, polymer C_{60}Pd_n grains and Pd nanograins. This explains the variety of forms of grains found in AFM image. The film with the medium content of Pd contains all these kinds of grains, except for palladium acetate and nanographite grains. This film is more uniform in topography and morphology, which can be connected with the fact that each grain observed by SEM and AFM is a kind of composite containing fullerenes grains, palladium acetate, polymer C_{60}Pd_n grains and Pd nanograins. Films with the highest Pd content have the most flat and the most uniform surface. We can suppose that they are formed of very fine amorphous carbonaceous grains and Pd nanograins with the size of about 10nm which we found previously in TEM studies [6]. Our SEM and AFM results show also that the size of superficial grains is very low.

4. Conclusions

The properties of carbon films containing Pd nanograins (Pd–C films) are substantially influenced by their microstructure and morphology. It has also been recognized that the parameters of technological process also have strong influence on the structure and morphology of these films. The aim of this work was to find how molecular properties,

topography and morphology of Pd–C thin films prepared by PVD method are affected by technological and chemical parameters.

Concluding, we obtained in PVD process at least three kinds of Pd–C films by the manipulation of the process parameters. The content of palladium in all these films is different and strongly affects the topography and the morphology of these films. The main reason for such differences is the composition of grains forming the film. The film is flat and smooth when it is composed of amorphous carbonaceous grains with very small Pd grains. The film with medium content of palladium has a surface covered with a hillock-like grains in which a presence of C₆₀–Pd polymer chains was found by Raman and FTIR methods. The topography of films becomes more complicated when other compounds are incorporated into grains. The morphology of such films reflects a composition of the grain.

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