

# Decomposition of palladium acetate and C<sub>60</sub> fullerite during thermal evaporation in PVD process

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The mechanisms of thermal decomposition of evaporated material during Physical Vapor Deposition (PVD) process depend on the kind of evaporated material. Such parameters of PVD process as deposition rate, source temperature and deposition time should be carefully selected taking into account the properties of material. Deposited films can span the range of chemical compositions based on the source materials. The nanostructural carbon films in form of palladium nanograins embedded in various carbonaceous matrixes were obtained by thermal evaporation during PVD process from two separated sources containing C<sub>60</sub> fullerite and palladium acetate, both in a form of powder. The evaporation was realized by resistive heating of sources under a dynamic vacuum of 10<sup>-3</sup> Pa. The influence of decomposition path of evaporated materials on the film structure has been discussed. Prepared C-Pd films were characterized using thermo-gravimetric method, differential thermal analysis, infrared spectroscopy and X-ray diffraction. The influence of decomposition of Pd acetate and fullerite on the final film structure was also shown.

Keywords: *palladium acetate; fullerite; PVD; TGA*

## 1. Introduction

Physical Vapor Deposition (PVD) technique is a method of films preparation and it consists of three basic stages: vaporization of the material from a solid source, transportation of the vapor in vacuum to the substrate surface and condensation onto the substrate to generate a film [1, 2]. Very often, the PVD technique, in order to intensify the process, is assisted by ionization of gases and vapors of metals by an additional glow discharge, the use of different physical fields (fixed or variable electric or magnetic field, additional source of electrons), heating the substrate or the use of additional reactive gases [3–5].

Fullerenes are electrochemically active in the negative potential range due to their relatively good electron-accepting ability [6, 7]. Therefore, fullerene-based polymers can be used as n-doped materials. Fullerenes are attractive as building blocks for polymers. Incorporation of fullerene moieties into other polymeric structures is also

possible. Fullerene derivatives can be covalently incorporated in polymeric network as pendant substituents into side chain of polymer or can form main backbone of polymeric structure [8].

The reactions of transition metal complexes with fullerenes result in formation of an interesting array of new compounds. Some of the reactions lead to formation of new complexes by addition of ligating groups to the fullerene so that the metal center is attached to the fullerene through some type of bridging arrangement [9]. An example could be a C<sub>60</sub>-Pd polymer in which fullerene moieties are covalently bonded to transition metal atoms or their complexes to form a polymeric network [10].

Another important factor in our technique of preparing C-Pd films is the catalytic activity of palladium [11, 12].

During thermal evaporation in PVD process, nucleation and agglomeration of nanoparticle aggregates can occur in dispersed phase, not only on the substrate, for example, in the method of pulsed plasma in which the nucleation occurs in the plasma [13].

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In our previous papers [14, 15] the influence of technological parameters of PVD process on the morphology, topography and crystal structure of C-Pd films was discussed. In this paper, we have shown that a nanocomposite film containing Pd nanograins embedded in a carbonaceous matrix is formed as a result of evaporation of C<sub>60</sub> fullerite and palladium acetate. The mechanisms of thermal decomposition of evaporated material (C<sub>60</sub> fullerite and palladium acetate) during PVD process and the influence of decomposition path of evaporated materials on the C-Pd film structure have been studied.

## 2. Experimental

To investigate decomposition of palladium acetate and C<sub>60</sub> fullerite during thermal evaporation in PVD process, the following research activities were performed: thermogravimetric analysis of palladium acetate and C<sub>60</sub> fullerite, next evaporation of palladium acetate in a PVD process and then investigation of the structure and topography of obtained coatings.

Nanocomposite C-Pd films were obtained by PVD process using two starting materials: fullerite C<sub>60</sub> and palladium acetate, both placed in separate sources and heated resistively. The temperature of the sources depended on the intensity of electric current, which was a parameter characterizing every process. The processes were carried out in dynamic vacuum ( $10^{-3}$  Pa). The fused silica substrate was placed at a distance of  $d = 60$  mm away from the source. Palladium (II) acetate Pd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> and fullerite C<sub>60</sub> (99.99 %) were purchased from Sigma-Aldrich. Thermogravimetric analysis was performed using SDT Q600 TA Instruments in the temperature range of 50 °C to 1000 °C at the heating rate of 10 °C/min and at the gas flow rate of 100 mL/min. C-Pd films for the thermal studies were mechanically removed from the substrate. The measurements were carried out in argon and in air. The study in argon was performed to get information on thermal decomposition of palladium acetate and C<sub>60</sub> fullerite in the conditions similar to those which were in the chamber in the PVD process. The results obtained in the air atmosphere

allowed us to observe oxidation of palladium, combustion of organic residues of acetate and formation of carbon monoxide and carbon dioxide from carbonaceous matrix. Strength and thermal resistance of C-Pd films in air is also important in view of their possible applications, for example as hydrogen sensor.

The thermal decomposition reaction and characterization of the products were investigated by thermogravimetric (TG) and differential thermal analysis (DTA). The data were also presented as a derivative thermogravimetric (DTG) curve, which is a plot of the rate of mass change with respect to temperature. The DTG mass losses are plotted downward and the gains upward.

The molecular structure of Pd and Pd-C films was investigated by infrared spectroscopy with Fourier transformation (FT-IR). Energy dispersive X-ray spectrometry method was used to analyze the composition of the films. X-ray diffraction (XRD) technique was applied to study the crystal structure of obtained films before and after TG measurements. XRD data were collected at room temperature in the  $\theta/2\theta$  scanning mode with CuK $\alpha$  radiation using Si(Li) semiconductor detector. The topography and composition of the PVD films were studied by scanning electron microscopy (SEM). Qualitative and quantitative analysis of the composition of C-Pd films was done using the Energy Dispersive X-ray Spectroscopy (EDX) technique.

## 3. Thermal decomposition of palladium acetate and C<sub>60</sub> fullerite

Fig. 1 shows the results of thermogravimetric analysis (TG green line), derivative thermogravimetric analysis (DTG – blue line) and differential thermal analysis (DTA – red line) of decomposition of palladium acetate in argon and in air at heating rates of 10 °C/min.

The TG analysis exhibits that the decomposition of Pd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> in both gases takes place in a single step accompanied by an exothermic peak at the temperature of  $\sim 250$  °C corresponding to the formation of Pd metal and volatile products.

The beginning of the decomposition can be considered at a temperature of 180 °C and the end of the process at 260 °C. The weight loss is estimated to be about 53 % of the total weight in argon and 56 % in air. The theoretical values for the weight loss on conversion of palladium (II) acetate to palladium (II) oxide and palladium metal are 45.48 % and 52.60 %, respectively [16].

After the decomposition to elemental palladium, further heating in air leads to a slow oxidation to form palladium (II) oxide (PdO). At heating rates of 10 °C/min, the weight increase starts around 413 °C. This oxidation is evident in the TG curve as the weight gain of about 4 %. The palladium (II) oxide can be reduced back to the metal by heating beyond 800 °C. As a result, in the range of 812 °C to 836 °C, the weight loss is about 7.6 %. The total weight loss during heating in air to 1000 °C is ~56 %. Additionally, the DTA curve shows that the reaction of palladium oxide decomposition process is endothermic.

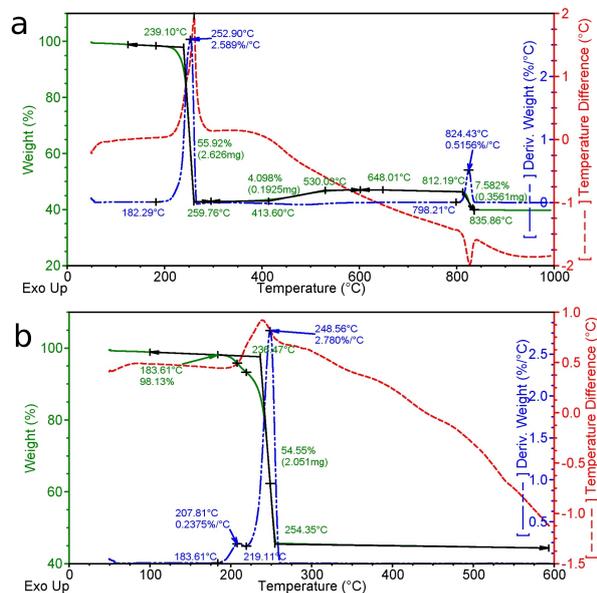


Fig. 1. Thermal analysis of palladium (II) acetate (a) in argon; (b) in air. TG – green line, DTG – blue line, DTA – red line.

Thermal decomposition of  $C_{60}$  fullerite occurs in the temperature range depending on the gas used. Evaporation of degradation products of  $C_{60}$  fullerite in argon (Fig. 2a) takes place

in the temperature range of 550 °C to 800 °C. This process is endothermic with the 97 % loss of weight and with maximum of DTG at 783 °C.

In case of heating in air, the  $C_{60}$  fullerite oxidation process takes place. In Fig. 2b we can observe that the weight loss of fullerite in air starts at lower temperature than in argon, ~400 °C. This process is strongly exothermic. The temperature of the maximum rate of mass loss (peak DTG) is ~580 °C. At 600 °C the weight loss is 99 %.

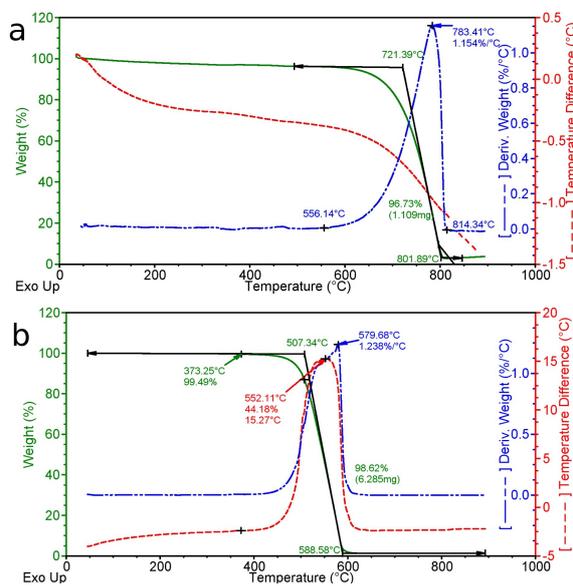


Fig. 2. Thermal analysis of  $C_{60}$  fullerite (a) in argon; (b) in air. TG – green line, DTG – blue line, DTA – red line.

#### 4. Decomposition of palladium acetate during thermal evaporation in PVD process

In order to analyze the decomposition of palladium acetate during thermal evaporation in vacuum, three PVD processes were carried out at different temperatures. Palladium acetate was placed in a molybdenum container and led to evaporation by resistance heating. The temperature of the source depended on intensity of electric current. The resistance of source containing palladium acetate was changed by changing the current intensity

Table 1. Technological parameters of Pd-films obtained in PVD process and EDX analysis results.

|      | I <sub>Pd</sub> [A] | Temp. of substrate [°C] | EDX spectrum |     |      |      |        |
|------|---------------------|-------------------------|--------------|-----|------|------|--------|
|      |                     |                         | C            | O   | Si   | Pd   | Total  |
| Pd-1 | 0.9                 | 47                      | 21.9         | 9.2 | 40.1 | 28.8 | 100.00 |
| Pd-2 | 1.1                 | 91                      | 9.7          | 1.8 | 59.1 | 29.4 | 100.00 |
| Pd-3 | 1.3                 | 111                     | 9.6          | 1.2 | 16.4 | 72.8 | 100.00 |

from 0.9 A to 1.3 A. During such process, the temperature of the substrate was registered. The technological parameters of such PVD processes and results of EDX analysis are shown in Table 1.

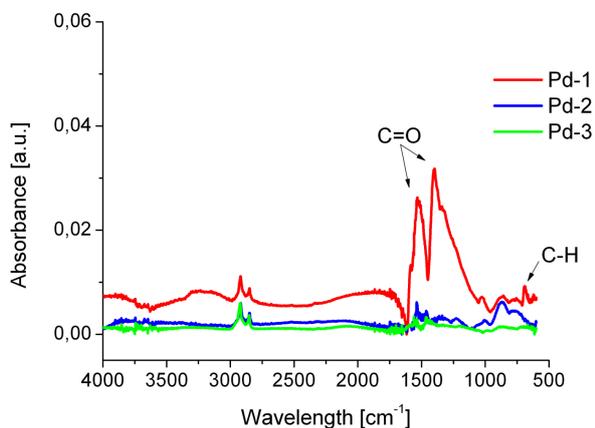


Fig. 3. FT-IR spectra of Pd films obtained by PVD process.

Analyzing EDX spectrum we can find that the Pd-1 film obtained at low temperature is composed of palladium, carbon and oxygen. This indicates that this process occurred with partly decomposed palladium acetate. This conclusion is confirmed by FT-IR spectra of prepared films. In case of two next films the content of carbon is less than 10 %.

The study of molecular structure of the films by infrared spectroscopy with Fourier transform showed that in the process carried out at the lowest intensity of current of the resistively heated source containing palladium acetate (Pd-1 film), only partial decomposition of palladium acetate took place. The FT-IR spectrum of Pd-1 film (red line in Fig. 3) shows the band attributed to the vibration of carbonyl group of palladium acetate at wave numbers: 1605 cm<sup>-1</sup>, 1432 cm<sup>-1</sup> and 695 cm<sup>-1</sup>.

In case of Pd-2 (blue line) and Pd-3 (green line) films, the bands characteristic of palladium acetate are not found.

The topography of Pd-films is shown in SEM images in Fig. 4. Pd-1 film, consisting of organometallic compounds has a smooth surface and low conductivity. In case of next Pd-films we observe an increase in surface roughness. On the surface of Pd-3 film, granular structure is visible.

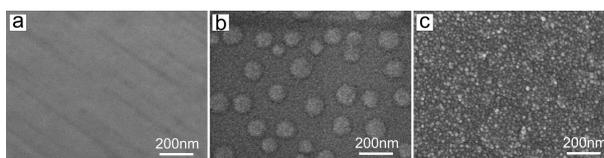


Fig. 4. SEM images (a) Pd-1; (b) Pd-2; (c) Pd-3

The XRD studies showed that for first sample no palladium particles with metallic character were observed (Fig. 5). The band that may be derived from locally ordered molecules of acetate residues is seen in the diffraction pattern of Pd-1 film (red line). In the XRD spectra of Pd-2 and Pd-3 films, obtained at higher temperatures, peaks corresponding to metallic Pd of fcc type structure are observed. In the event of the Pd-2 film (blue line) a peak attributed to the (1 1 1) plane of palladium is seen. For Pd-3 film (green line) additional peak from the plane (2 0 0) is observed. This is connected to an increase in the number and size of Pd nanograins. High temperature process led to degradation of palladium acetate to metallic palladium and subsequent evaporation of the metal clusters or particles. Sublimation of palladium with only partial acetate decomposition occurred during the deposition of Pd-1 film.

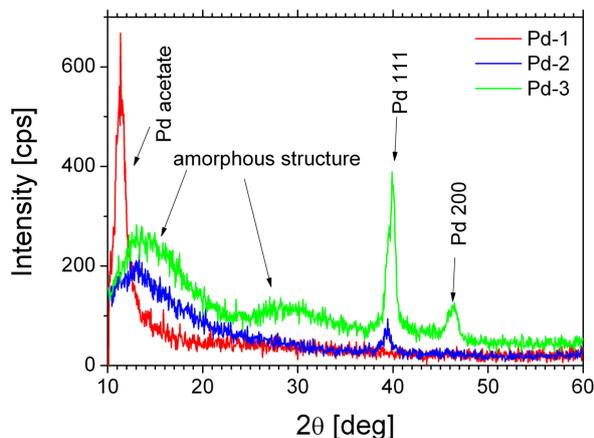


Fig. 5. X-ray diffraction patterns of Pd films obtained by PVD process.

## 5. Thermal decomposition of C-Pd films evaporated in PVD processes

The PVD processes of C-Pd films preparation were carried out at the same temperature of source containing  $C_{60}$  fullerite. The current of the source containing palladium acetate was 1.0 A and 1.1 A. The films were prepared on fused silica plates. Table 2 presents technological parameters of PVD processes in which the C-Pd films were obtained, and composition of the films obtained from qualitative and quantitative EDX analysis.

EDX results show that the C-Pd 1 film is composed predominantly of carbon and about 10 wt.% of palladium. For C-Pd 2 film, we can observe a twofold increase in palladium content and a decrease in carbon content.

In order to examine the molecular structure of C-Pd films, FT-IR spectra were analyzed. Fig. 6 presents the FT-IR spectra of C-Pd films. In the spectrum of C-Pd 1 film the bands characteristic of vibration of molecules of fullerene  $C_{60}$  ( $1183\text{ cm}^{-1}$ ) and palladium acetate ( $1594\text{ cm}^{-1}$ ,  $1427\text{ cm}^{-1}$  and  $698\text{ cm}^{-1}$ ) are visible. No characteristic bands of palladium acetate and fullerene for C-Pd 2 film are observed. Higher temperature of the source of Pd acetate for C-Pd 2 film than for C-Pd 1 resulted in the total decomposition of this compound. The catalytic properties of Pd nanoparticles can cause faster decomposition of  $C_{60}$  grains.

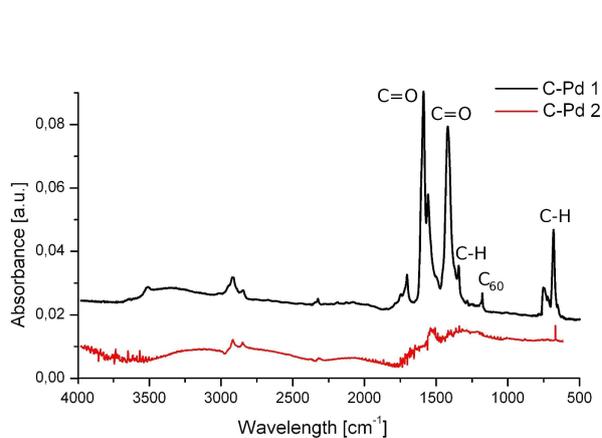


Fig. 6. FT-IR spectra of C-Pd films

The change in the current of the source containing palladium acetate caused a change in substrate temperature which affected the topography of the films. SEM image of C-Pd 1 film (Fig. 7a) shows that the film surface is very smooth and homogeneous. The topography of C-Pd 2 film (Fig. 7b) is different from the topography of C-Pd 1 film. The entire surface of the film is coated with large islands with a diameter of 50 nm to 200 nm.

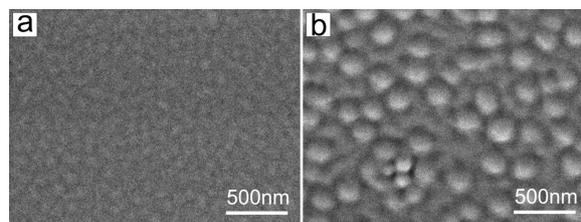


Fig. 7. SEM images of C-Pd films (a) C-Pd 1; (b) C-Pd 2

TG/DTG/DTA curves of C-Pd films obtained in air atmosphere are presented in Fig. 8. The TG analysis of C-Pd 1 film has shown the weight loss of this sample in the temperature range of  $150\text{ }^{\circ}\text{C}$  to  $400\text{ }^{\circ}\text{C}$  (Fig. 8a). Mass loss observed in this temperature range is 60 %. DTG curve clearly shows two peaks. The first maximum rate of decomposition occurred at  $\sim 306\text{ }^{\circ}\text{C}$  and the second at  $\sim 347\text{ }^{\circ}\text{C}$ . Both processes are exothermic as evidenced by the two peaks on the DTA curve. At the temperature of  $\sim 490\text{ }^{\circ}\text{C}$  the weight increases due to oxidation and between  $810\text{ }^{\circ}\text{C}$  to  $825\text{ }^{\circ}\text{C}$ , above 7 % mass loss is visible.

Table 2. Technological parameters of prepared C-Pd films in PVD process and results of EDX analysis.

| Sample | Evaporation intensity |          | Substrate temperature [°C] | EDX spectrum |      |      |      |
|--------|-----------------------|----------|----------------------------|--------------|------|------|------|
|        | IPd [A]               | IC60 [A] |                            | C            | O    | Si   | Pd   |
| C-Pd 1 | 1                     | 2        | 76                         | 62.5         | 13.1 | 14.2 | 10.2 |
| C-Pd 2 | 1.1                   | 2        | 82                         | 39.7         | 15.5 | 19.9 | 24.9 |

Thermogravimetric analysis of C-Pd 2 film is presented in Fig. 8b. As in the previous sample we can observe the mass loss at similar temperature range of 180 °C to 400 °C. The weight loss is ~20 %. The decomposition is clearly a multi-stage process with DTG<sub>max</sub> at 205 °C, 243 °C, 302 °C, 353 °C, 371 °C. At a temperature of 800 °C a rapid weight loss (above 8 %) is visible. In the event of decomposition of palladium oxide in thermal analysis of palladium acetate, the mass loss is ~7.6 %. Greater weight loss in C-Pd film indicates that in this film the components of carbon matrix were also oxidized.

The mass loss of C-Pd films begins at the lower temperatures and has less rapid course than decomposition of palladium acetate.

Total mass loss of C-Pd 2 film is more than twice less than in C-Pd 1 film obtained at a lower temperature process, comprising a plurality of organic residues from acetate. Carbon present in the C-Pd films occurs in the form of amorphous carbon fullerene molecules or a structure of local graphite order. The loss of mass may be associated with the combustion of new forms of carbon created during PVD process by heating in vacuum and sublimation of partially decomposed palladium acetate. Due to catalytic properties of palladium in C-Pd films the new form of carbon palladium structures can also be formed, which could affect the thermal decomposition.

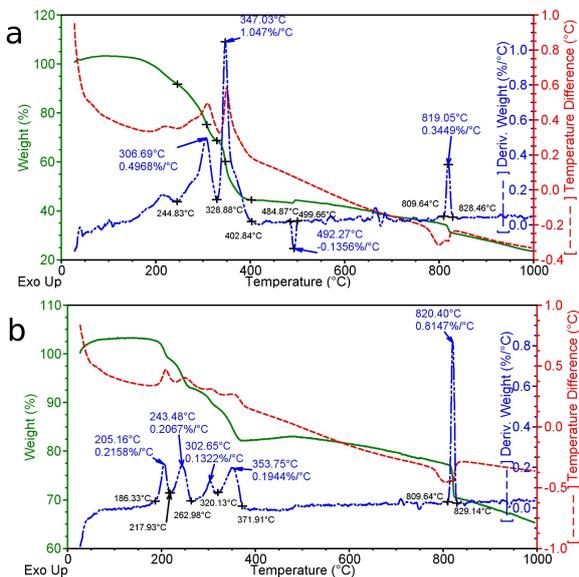


Fig. 8. Thermal analysis of C-Pd films in air, TG - green line, DTG - blue line, DTA - red line. (a) C-Pd 1 film; (b) C-Pd 2 film.

The differences in the thermal decomposition of the C-Pd films in comparison with the decomposition of precursor films are significant. The mass loss in the temperature range of 270 °C to 470 °C cannot be attributed to any of the precursors.

## 6. Conclusions

In this paper, the studies of simultaneous evaporation of C<sub>60</sub> fullerite and palladium acetate in PVD process (from two independent sources) have been presented. Such simple and cheap method allowed us to obtain a film composed of palladium nanograins with crystal structure (fcc type) embedded in a matrix composed of different allotropic forms of carbon.

C-Pd films obtained in PVD process with different parameters have different structures, topographies and morphologies, and their thermal decomposition occurs at different temperatures.

We have also shown that in the PVD processes, in which one source with lower temperature is used for evaporation of palladium acetate, palladium acetate starts to sublime with partial decomposition to metallic particles. Thus, in the study of molecular structure of these films, the bands of carboxyl

groups and methyl are visible. Higher temperatures of PVD process cause palladium acetate to decompose to metallic form during heating in the source followed by evaporation of the metal.

We suppose that the effect of the catalytic activity of palladium during the PVD process results in degradation of fullerene molecules.

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