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Characterization of Palladium-based Thin Films Prepared by Plasma-enhanced Metalorganic Chemical Vapor Deposition

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The plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD) was used to prepare palladium–based thin films starting with palladium (II) acetylacetonate precursor ($Pd(acac)_2$) mixed with argon (carrier gas). To characterize chemical structure and morphology of deposited films Raman spectroscopy and electron diffraction techniques were used. The energy dispersive X-ray microanalysis (EDX) was applied to specify composition of films. The film thickness was estimated by ellipsometric measurements.

The obtained results show that the films have various composition depending on deposition parameters. It has been found that the thermal decomposition at 623 K of the films leads to the formation of fine 5 nm – 10 nm size palladium nanoparticles, to which the catalytic activity is attributed.

Keywords: plasma deposition, thin palladium film, Raman spectroscopy, electron diffraction.

1. INTRODUCTION

Plasma-enhanced metalorganic chemical vapor deposition (PEMOCVD) is well-known deposition method to obtain thin films [1 – 3]. Moreover, it can produce single layers, composites, nanostructured and functionally graded coating materials with a well-controlled dimension, unique structures and properties at low processing temperatures [4]. In recent years, the application of this technique to produce supported nano-sized catalysts has received growing attention because aggregations of the catalytic clusters caused by high temperatures of calcination processes might be avoided [5].

Several groups have used the plasma deposition method to prepare thin catalytical films. In many cases the received results of catalytic activity and selectivity are very promising. For example, Koyano et al. [6], prepared a cobalt oxide catalyst, using $Co(OCOCH_3)_2$ and oxygen plasma, with higher dispersion and higher catalytic activity in the oxidation of CO and propane than those typical of CoO_x catalysts prepared by wet chemical methods. Karches et al. [7] showed that the plasma-deposited thin films of TiO_2 (with thickness of 7 nm – 120 nm) demonstrate efficiency of the photodecomposition of oxalic acid comparable with a commercial catalyst. Łojewska et al. [8], presented that the plasma deposited cobalt oxide on chromium-aluminum steel carriers of designed geometry were regarded as a possible alternative for monolithic converters for VOC combustion. A few other materials with potential catalytic properties, such as thin films of MoO_x, Pt, and CrO_x/La_2O_3-ZrO_2 have been recently prepared with success by the PEMOCVD method [9 – 11].

Referring to those observations, we make an attempt to produce palladium-based thin films which can be applicable in catalysis. This paper focuses on the synthesis and characterization of the mentioned thin films, obtained by PEMOCVD method. The manufactured films were characterized by Raman spectroscopy and electron diffraction techniques. Based on the Scherer equation adapted to electron diffraction [12] crystalline size was evaluated. To estimate the composition of the films the energy dispersive X-ray microanalysis (EDX) was applied. Ellipsometric measurements were used to determinate the film thickness. The additional thermal decomposition was applied after plasma processing to create nanoclusters of Pd in the deposited films.

2. EXPERIMENTAL PART

2.1. Deposition of the films

The parallel plate radio frequency (R.F. 13.56 MHz) plasma reactor used for deposition palladium–based thin films is schematically shown in Fig. 1. The carrier gas was introduced through the mass flow controller to the heated container where it was mixed with precursor vapor, sublimated at the specified temperature. Then the obtained mixture was brought into a reactor chamber via a perforated grounded electrode. All gas lines and both electrodes were heated to 433 K in order to prevent condensation of the precursor.

To produce films (20 nm – 120 nm thick) we used palladium(II) acetylacetonate ($Pd(acac)_2$ Sigma-Aldrich 99 %) yellow powder under standard condition with vapor pressure 0.1 hPa at 433 K as the precursor, argon with purity 99.999 % as the carrier gas and the total pressure in the reactor chamber approx. 4.5 Pa. Flow rates of $Pd(acac)_2$ were regulated by the change of the sublimation temperature with fixed flow of argon 0.71 sccm (standard cm^3min^{-1}). The glow discharge power was 40 W.

As a substrates, glass plates with evaporated thick Au layer (for Raman spectroscopy and ellipsometric

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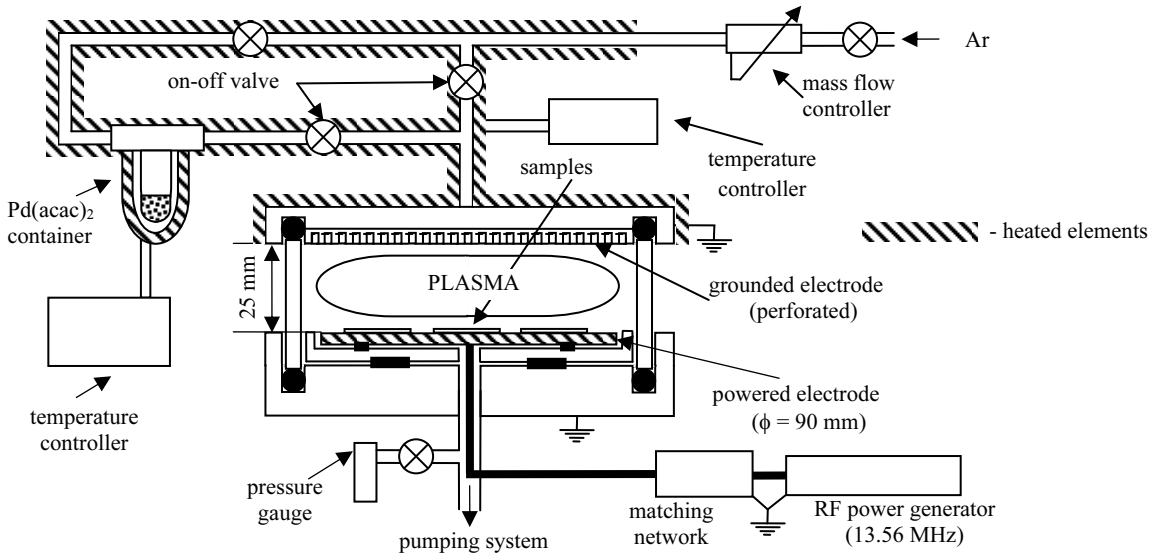

Fig. 1. Schematic diagram of the RF plasma reactor

measurements) and thin copper foil (for EDX analysis) were used. For electron diffraction measurements the films were deposited on thin (0.1 nm – 0.2 mm) NaCl plates. Then, the films were detached from the substrate by treatment with distilled water and transferred onto copper grids.

The samples always were prepared in double quantity at the same deposition time, because half of them were submitted to thermal decomposition at the temperature 623 K for 900 s.

2.2. Characterization of the films

The chemical structure and morphology of deposited films was investigated by Raman spectroscopy and electron diffraction technique. Raman spectra were obtained by a Jobin Yvon Raman spectrometer T64000, equipped with a microscope. As a source of light, an argon laser ($\lambda = 514.5$ nm) was used. All measurements were taken at the room temperature and the integration time for every single spectrum was equal to 720 s. Electron diffraction was performed by a transmission electron microscope with an electron diffraction mode (Jeol JMM-12EXI). The average crystallite size of the films was determined using modified Scherer equation (Eq. 1) from the Pd(111) electron diffraction peak.

$$L = \frac{K \cdot d_{hkl} \cdot D_{hkl}}{2 \cdot b}, \qquad (1)$$

where: L is the crystallite size; $K = 0.9$, which is the Scherer approximate constant related to the shape and index (hkl) of the crystals; d_{hkl} is the interplanar spacing; D_{hkl} is the diameter of the (hkl) diffraction ring; b is the corrected full width at half-maximum (FWHM) determined by Gaussian fitting of the electron diffraction pattern. The effect of geometric (instrumental) broadening on the electron diffraction peaks was calibrated.

To characterize the composition of the films, scanning electron microscopy with energy dispersive X-ray microanalysis (SEM-EDX FEI Quanta 200F with Oxford Instruments detector X-Max50) were used.

The thickness of the produced films was measured by a null ellipsometer Rudolf 431A working at an incident light wave of 632.8 nm.

3. RESULTS AND DISCUSSION

Several attempts have been taken to find optimal sublimation temperature of our precursor compared to good dispersion of palladium inside the films. Each time we carried out the EDX analysis to find total content of palladium. To confirm the homogeneity of the layers EDX analysis was performed at ten different points. The most important results are summarized in Table 1. As one can see, with an increasing temperature of sublimation higher than 413 K, on our deposition system, we obtain films rich in carbon with a small content of palladium even after thermal decomposition in 623 K for 900 s. In turn, at the temperature lower than 413 K the total content of palladium is very low and the obtained films are not uniform. Since the films are to be produced for the use in catalysis [13 – 15], the greatest possible amount of catalytically active material is desirable. Therefore, for subsequent investigations, we chose temperature 413 K. Under those conditions the obtained films had required good homogeneity and the highest content of palladium with growth rate ca. 0.25 nm s^{-1}. The thickness of the films as a function of the deposition time was linear as shown in Fig. 2.

Fig. 3 presents a typical TEM micrograph (a) and selected-area electron diffraction (SAED) pattern (b) of the deposited palladium-based thin films without thermal decomposition. It can be seen that films are uniform without any crystalline structures. SAED indicates that obtained films are amorphous and no distinct peaks are observed. After thermal decomposition at 623 K for 900 s on air, which is the accepted procedure for obtaining nanostructures with likely catalytic properties from the amorphous layers [16], films show crystalline pattern (Fig. 4, b) and the observed diffraction lines match the reported values for the cubic Pd phase, as shown in Table 2.

Table 1. Dependence of the palladium contents on sublimation temperature $Pd(acac)_2$ obtained by EDX

No	Temp. of subl. $Pd(acac)_2$ (K)	Pd (at%)	C (at%)	O (at%)	Pd (at%)	C (at%)	O (at%)
		without thermal decomposition			after thermal decomposition		
1	403	0.855	92.347	6.798	1.007	61.706	37.287
2	413	4.323	88.884	6.793	5.093	58.429	36.478
2	423	2.061	92.014	5.925	2.441	60.482	37.077

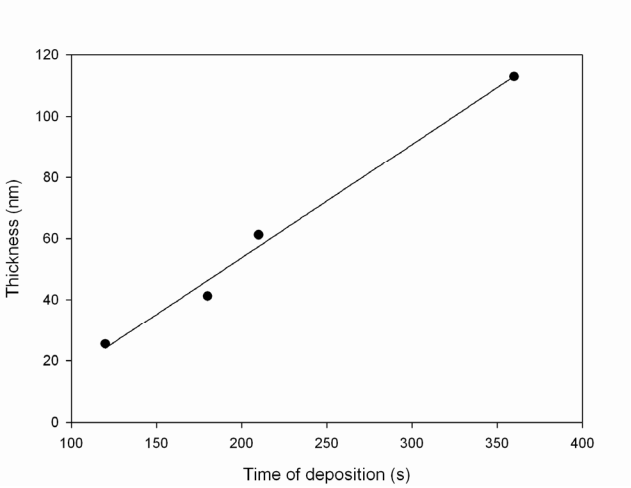

Fig. 2. The thickness of palladium-based films as a function of the deposition time

Table 2. Electron diffraction data for the palladium-based film deposited by PEMOCVD and for a typical cubic Pd phase

No.	hkl	Typical cubic Pd [17]		Our results	
		d (Å)	Intensity (%)	*d* (Å)	Intensity (%)
1	111	2.24580	100	2.245	100
2	200	1.94511	60	1.934	70
3	220	1.37537	42	1.370	50
4	311	1.17295	55	1.166	40
5	222	1.12298	15	–	–
6	400	0.97254	13	–	–
7	331	0.89248	40	–	–
8	420	0.86988	11	–	–

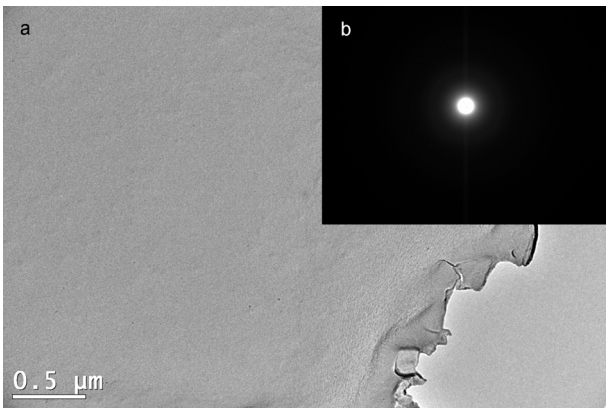

Fig. 3. TEM micrograph (a) and SAED pattern (b) of Pd-based films

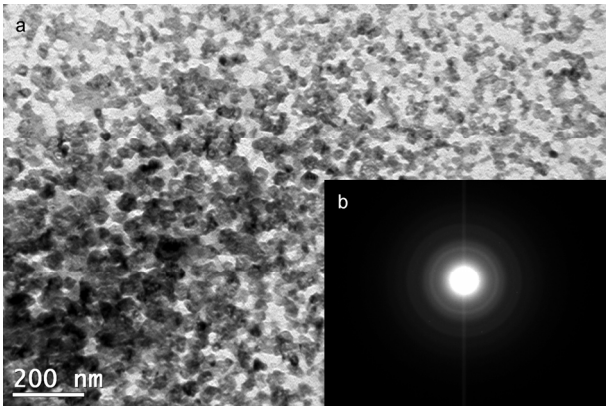

Fig. 4. TEM micrograph (a) and SAED pattern (b) of palladium nanoparticles after thermal decomposition

We do not observe all the lines derived from palladium, which is probably associated with remaining on the layer large amount of amorphous carbon.

The average diameter of the Pd nanoparticles estimated according to Eq. 1 is 8 nm. TEM micrograph Fig. 4, a, reveals that the Pd nanocrystals are spherical and well dispersed. The observed size of the particles ranges from 5 nm to 10 nm, which is in good agreement with the size estimated by the modified Scherrer equation from the electron diffraction pattern.

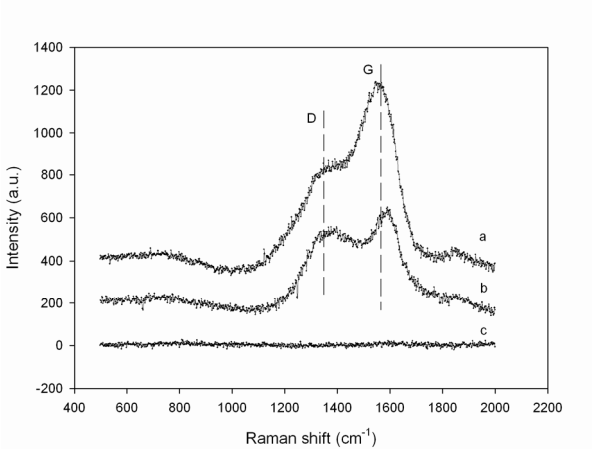

Fig. 5. Raman spectra of the films before thermal treatment (a), after treatment at 623 K for 900 s (b), after treatment at 673 K for 900 s (c)

To determine the chemical structure of the Pd-based films, Raman spectroscopy measurements were performed. Typical spectra before and after thermal decomposition of the films are shown in Fig. 5. One evident region can be observed between 1200 cm^{-1} and 1800 cm^{-1} assigned to carbon structures. The two bands centered at about 1360 cm^{-1} and 1570 cm^{-1} correspond to the disordered graphite D line and the typical graphite G line, respectively

[18]. Thermal decomposition at 623 K for 900 s produced decreasing intensity of observed bands, which is connected with the reduced contents of carbon, confirmed by EDX analysis. Because the burnt layers still contain a large amount of amorphous carbon (which can also be seen in Fig. 4, b) another sample was subjected to thermal decomposition at 673 K for 900 seconds, which led to a complete removal of carbon observed by Raman spectroscopy (Fig. 5, c). Additional studies, however, are necessary to determine the extent to which the carbon fraction is removed.

4. CONCLUSIONS

This paper provides evidence that PEMOCVD is a very useful method to produce thin films containing palladium from the mixture of $Pd(acac)_2$ and argon. Investigations performed by electron diffraction prove that obtained films are amorphous and after thermal decomposition at 623 K for 900 s nanocrystalline clusters of Pd with size of 5 nm – 10 nm are formed. This observation was confirmed by TEM micrographs which showed that the produced films have homogeneity with good dispersion of palladium. The Raman spectroscopy and EDX analysis display that contents of carbon fraction after thermal decomposition is decreased. Further studies should be focused on the optimization of the deposition process to fabricate films with the highest concentration of palladium and carry out a catalytic test to find probable catalytic properties. Although the films discussed in this paper are far from the perfection, the received promising results have inspired us to continue the investigations on palladium-based films produced by the PEMOCVD method.

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