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Nanostructured C–Pd films for hydrogen applications

Anna Kamińska, Ryszard Diduszko, Elżbieta Czerwosz, Ewa Kowalska*,
Mirosław Kozłowski

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

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ABSTRACT

We propose nanostructured carbonaceous-palladium (C–Pd) films as promising material for covering different, big surfaces as improving hydrogen storing properties material. The C–Pd films were obtained by annealing of samples prepared by physical vapor deposition on fused silica substrates. Palladium nanocrystallites placed within the film volume and also on its surface enhanced absorption of hydrogen due to dissolution of H₂ molecules in the nanocrystallites. We studied structure, morphology and topography of these films by different methods (XRD, GIXRD, SEM and EDS). XRD measurements performed in situ under H₂/N₂ atmosphere showed that α phase and β phase of palladium hydride were formed.

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Introduction

Recently new alternative energy sources are still being searched in order to replace fossil fuels. Hydrogen is an energy carrier with great potential to become a major fuel for vehicles and stationary power generation. Hydrogen is an environmentally friendly substance because energy conversion process with H₂ is clean, only water vapor is formed as final product. Hydrogen can be stored in the form of gas, cryogenic liquid or adsorbed gas in solid materials [1,2]. Hydrogen storage in solid materials can be realized by chemical reaction with various metals or metal alloys [2,3]. Hydrogen storage materials can be divided into two classes depending on the hydrogen sorption mechanism: materials in which only

physisorption take place or materials in which absorption is due to chemisorption [4]. In case of physisorption molecular hydrogen is weakly bound to the adsorbent surface by van der Waals bonds. The adsorption process is fast, and fully reversible. In case of chemisorption hydrogen molecules dissociate to hydrogen atoms which can form ionic or covalent bonds with the material. These bonds are much stronger than bonds of van der Waals, so hydrogen desorption can be incomplete.

Presently, metal hydrides [5] or carbon nanoporous structure [6–9] is promising materials at which hydrogen can be stored. Microporous carbon such as activated carbon, carbon nanofibers, nanotubes and other carbon nanostructures (foam, graphite) is attractive candidates for hydrogen storage due to their light weight, high surface area, chemical stabilities and also high porosity.

* Corresponding author. Tel.: +48 22 635 86 28; fax: +48 22 831 92 31.

E-mail address: ewa.kowalska@itr.org.pl (E. Kowalska).

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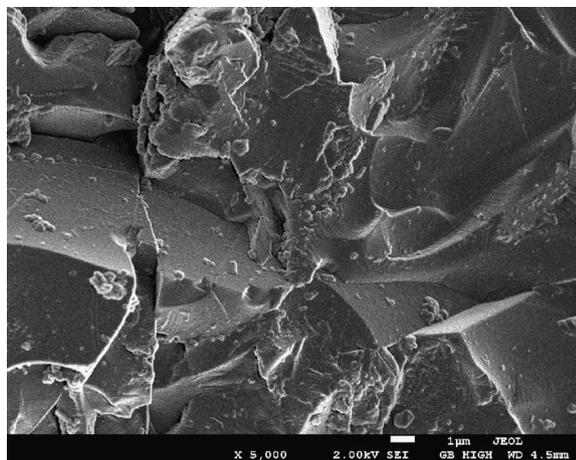


Fig. 1 – SEM micrograph of film obtained on fused silica in PVD process.

Among hydrides, palladium is an element usually taken into consideration due to its high ability to absorb hydrogen [10,11]. The metal acts as an activator of hydrogen by reversibly dissociating into metal-H atom. As a result palladium hydride PdH_x is formed. Depending on the value of absorbed hydrogen (x), palladium hydride can occur in two different phases. At low H_2 concentration ($x < 0.02$) a solid solution (α phase) is formed. When hydrogen concentration increases and x is between 0.02 and 0.6 the second phases (β phase) appears and coexist with α phase. Further increase of H_2 concentration resulting in disappearing of α phase and only β phase remains [12]. The hydrogen solubility in palladium nanoparticles is much greater compared to the bulk material.

In this work we present the carbonaceous – palladium (C–Pd) films which can be used as potential hydrogen storage material. These films were deposited on fused silica substrates using physical vapor deposition (PVD) process and next annealing of PVD films at different temperatures in the range from 500 °C to 700 °C in argon gas at the same time of

30 min. SEM studies show that Pd nanoparticles due to temperature get out on the surface of the films what enhanced the reaction between hydrogen-palladium nanocrystals. Palladium nanograins present in nanostructured films are responsible for forming palladium hydride. On this basis we suggest that C–Pd films can be used as storage materials, although we should be aware that quantity of stored H_2 is small. Our materials can be applied as a container to store small amounts of hydrogen and also to fast absorption and desorption as well as to select of H_2 from gas mixture.

In our previous papers [13–17] we have described many properties such as electrical, morphological, topographical, hydrogen sensing and storage. These properties are dependent not only on the carbonaceous matrix structure but also on the size and structure of Pd nanocrystals embedded in the C matrix.

Experimental details

Preparation of C–Pd films

Nanostructured carbonaceous-palladium (C–Pd) films were prepared by physical vapor deposition (PVD) and then annealed under an argon atmosphere. Fullerene C_{60} and palladium acetate $\text{Pd}(\text{AOC})_2$ were precursors of the initial nanostructured C–Pd films in PVD process. Both compounds were evaporated on unpolished fused silica substrates from two separated sources with currents flowing through the sources: $I_{\text{C}_{60}} = 2.0$ A and $I_{\text{Pd}} = 1.2$ A. Duration time was 10 min and the distance between sources and substrates was 60 mm. As a result, C–Pd films with the thickness of about 300 nm were deposited. Then the films were annealed at different temperatures in the range from 500 °C to 700 °C in an argon flow rate of 40 L/h.

SEM and EDS characterization

The topography, morphology and structure of the prepared C–Pd films were analyzed by Scanning Electron Microscopy

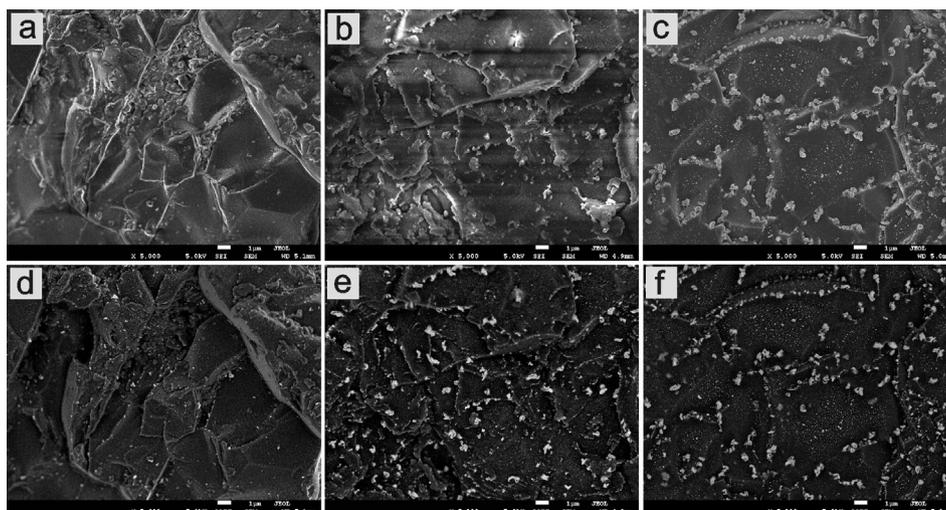


Fig. 2 – SEM micrograph of film annealed in a) 500 °C, b) 600 °C, c) 700 °C obtained in SE mode and d) 500 °C, e) 600 °C, f) 700 °C obtained in LAME mode.

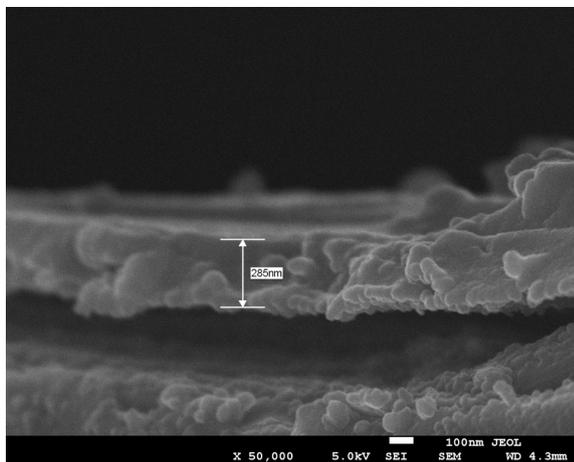


Fig. 3 – Cross-sectional SEM image of C–Pd film annealed at 700 °C.

(SEM) with the JEOL JSM-7600F field emission scanning microscope, with SE (Secondary Electron) and LBE (Low Angle Backscattered Electron) detectors. The quantitative analysis of C–Pd films was determined by energy-dispersive spectroscopy (EDS). The EDS measurements were performed with INCA ENERGY 250 using accelerating voltage of 7 kV using area scanning method.

XRD studies

In order to determine the C–Pd films hydrogen uptake capacity, X-ray diffraction (XRD) studies were performed on the W1 beamline at Doris III synchrotron at HASYLAB. GIXRD (Graazing Incidence X-ray Diffraction) measurement geometry with the 2° incident angle was used to enhance diffraction effects that are very weak because of low thickness of the studied films (~300 nm). A double Si (111) crystal monochromator provided radiation with a wavelength of $\lambda = 0.154056$ nm, equal to that of the $K_{\alpha 1}$ Cu fluorescence line, was used. The special cell was constructed to enable the flow

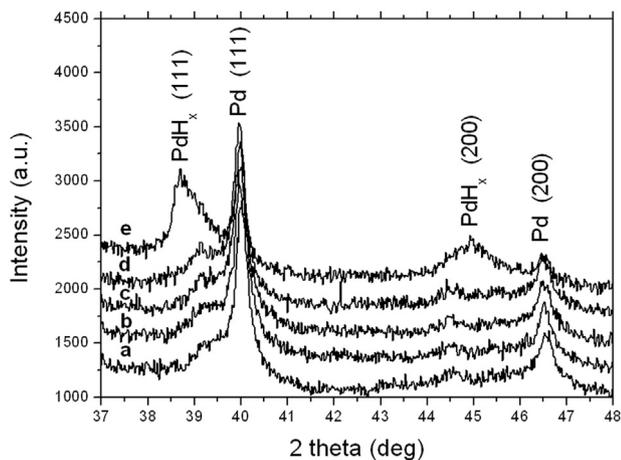


Fig. 4 – Diffraction patterns of the C–Pd film annealed at 500 °C under the H₂/N₂ atmosphere (a – 0% H₂, b – 0.5% H₂, c – 1% H₂, d – 2% H₂, e – 4% H₂).

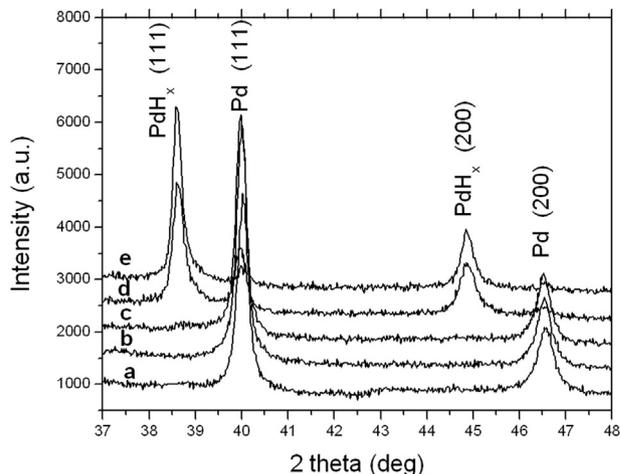


Fig. 5 – Diffraction patterns of the C–Pd film annealed at 600 °C under the H₂/N₂ atmosphere (a – 0% H₂, b – 0.5% H₂, c – 1% H₂, d – 2% H₂, e – 4% H₂).

of H₂/N₂ mixture for in situ diffraction measurements. The gas flow rate was maintained at 1 L/min with different concentration of hydrogen in the range from 1 vol.% to 4 vol.%.

Results and discussion

SEM and EDS studies

C–Pd films were formed on the surface of SiO₂ where grains of unpolished fused silica have a large roughness. The film which covers the surface of substrate in PVD process had a thickness about 300 nm and was presented in Fig. 1. Grains of substrate with difference size and shape characterized smooth edges.

After the annealing process in argon, the structure of the C–Pd films is changed depending on the temperature. The

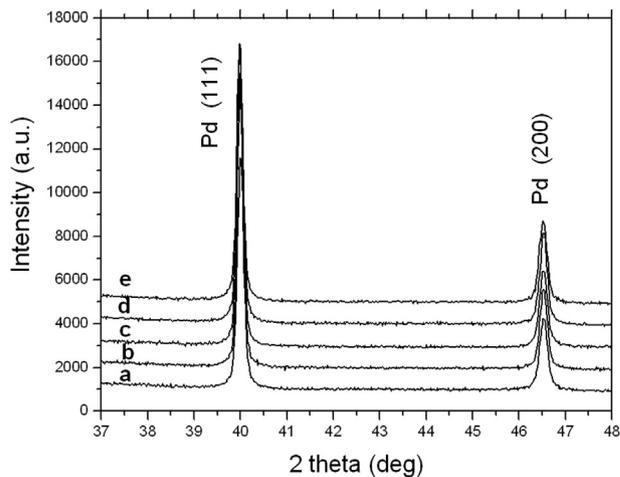


Fig. 6 – Diffraction patterns of the C–Pd film annealed at 700 °C under the H₂/N₂ atmosphere (a – 0% H₂, b – 0.5% H₂, c – 1% H₂, d – 2% H₂, e – 4% H₂).

Table 1 – Lattice constant of Pd/H crystals.

% H ₂ in H ₂ /N ₂ mixture	500 °C		600 °C		700 °C	
	Pd(H) α phase	PdH _x β phase	Pd(H) α phase	PdH _x β phase	Pd(H) α phase	PdH _x β phase
0	3.903		3.901		3.904	Not found
1	3.904		3.904		3.905	Not found
2	3.906		3.905		3.906	Not found
3	3.907		3.906	4.037	3.905	Not found
4	3.909	4.030	3.908	4.039	3.906	Not found

morphology of films which were annealed at 500 °C, 600 °C and 700 °C is shown in Fig. 2. In the films obtained in PVD process Pd nanograins are not visible because of their small size (a few nm) [18]. In the annealing process, Pd nanograins were coagulated in larger ones and were visible on the surface of unpolished fused silica substrate (Fig. 2). The size of Pd nanograins depends on the annealing temperature which is visible in Fig. 2.

It was observed that average size of nanograins Pd increased with increasing annealing temperature and after 500 °C was 25 nm and after 600 °C was 500 nm and after 700 °C was 630 nm.

The thickness of all films was similar. In Fig. 3 cross-sectional SEM image of C–Pd film annealed at 700 °C is presented. It can be seen that film thickness is about 300 nm.

The content of palladium in the C–Pd films was determined by EDS method. Due to the small thickness of the films (about 300 nm), EDS analysis was performed using an accelerating voltage of 7 kV to minimize X-ray excitation volume. EDS measurements showed that with increasing the annealing temperature decreased the thickness of the films due to the loss of carbon as a result of decomposition of precursors. The presence of precursors – C₆₀ and Pd(OAc)₂ was confirmed by FTIR and thermal analysis [14]. Therefore on the EDS spectra, intensity of PdL α line increased with growth of the annealing temperature. Additionally, intensity of the SiK α line from the substrate increases due to reduced thickness of the C–Pd films. In this situation, the amount of Pd in the films can be presented as the ratio of Pd/C. The calculated ratio of Pd/C for the films annealed at 500 °C, 600 °C and 700 °C is 0.18, 0.28 and 0.43, respectively.

XRD measurements

C–Pd films annealed at 500 °C, 600 °C and 700 °C, deposited on unpolished fused silica, were selected to research their behavior in hydrogen presence at different concentrations from 0 to 4 vol.%. Changes in the diffraction pattern during the process of absorption/desorption of hydrogen were observed in situ by using specially made measuring cell. It enabled the diffraction measurement of C–Pd films in the full range of incidence and reflection angles, with adjustable flow controlled gas mixture H₂/N₂. Results of these measurements are shown in Figs. 4–6.

In these studies we observed the formation of palladium hydride PdH_x β -phase in samples annealed at 500 and 600 °C but in the case of sample annealed at 700 °C palladium hydride was not formed. This result is likely due to the

graphite shells [19] which are formed around the Pd nanograins and hinder the hydrogen access into the Pd grains and also increase of grain sizes of Pd. Changes of lattice constant of α -phase of Pd(H) provide a high hydrogen absorption in C–Pd films annealed at 500 and 600 °C and weak absorption in the film annealed at 700 °C. Lattice constant of Pd/H crystals obtained from X-ray measurements are summarized in Table 1.

Conclusions

In this work nanostructured carbonaceous-palladium (C–Pd) films prepared by PVD method and annealed at different temperatures were studied. C–Pd films annealed at 500 and 600 °C can be used as hydrogen storage materials, although we should be aware that the quantity of stored H₂ is small. In these films α phase and β phase of palladium hydride were formed. The film annealing at temperature of 700 °C causes changes in the structure of C–Pd film resulting in deactivation of palladium grains on hydrogen absorption. This was connected with formation of graphite shells around Pd nanograins.

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