

33rd International Conference on Vacuum Microbalance and Thermoanalitical Techniques ICVMTT33 and 3rd COMPOSITUM Conference, Hybrid Nanocomposities and Their Applications **26-30 June 2011, Zamość**

Investigation of Pd content in C-Pd films for hydrogen sensor applications



E.Kowalska, E.Czerwosz, A.Kamińska, M.Kozłowski

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

INTRODUCTION

Hydrogen is a gas applied in many industry branches connected to hydrogenation process, chemical compounds production, cryogenic cooling, metallurgy processes and electronic devices exploitations. Continuous monitoring of the atmosphere composition near the hydrogen emission sources is necessary to preserve the industrial safety and to protect the human life. Recently, new technologies and materials to produce hydrogen sensors based on nanomaterials have been searched for.

In Tele- and Radio Research Institute the new technology of porous carbonaceous materials containing palladium grains (C-Pd films) to apply them to active layers in hydrogen sensors is developed. PVD process is used to obtain the initial films. Pd content and the size of Pd nanoparticles in carbon matrix are an important factor. It decides about H₂ absorption levels, thus about sensitivity of such type of the sensor. In this work we present how the distance changes in PVD synthesis method affects Pd content in carbonaceous materials.

SYNTHESIS METHOD

The initial film was obtained by PVD method using C_{60} powder and Pd(OAc)₂ as precursors of C-Pd films. As a result of both compounds

SEM CHARACTERISATION

SEM images (JEOL-JSM 7600F) of samples 1-3 are similar. All samples consist of carbonaceous grains in the size of 100nm. TEM studies prove that Pd nanoparticles with the size of 3-15nm are uniformly distributed in all volume of carbonaceous grains.

evaporation and next vapors condensation nanocomposite films containing carbonaceous grains and palladium nanoparticles with a diameter of 3-15 nm were formed. PVD process was performed under dynamic pressure at 10⁻⁵mbar. Technological parameters of PVD method i.e. the current through sources $(I_{C60}$ and $I_{Pd})$, the substrate-sources distance (d_{ss}) and deposition time (t) influence the films composition and structure. In our experiments only the distance d_{ss} was changed from 54mm (**sample 1**) through 60mm (sample 2) to 69mm (sample 3). Other parameters of PVD process were constant and were: $I_{C60}=2,1A$ for the fullerene source, $I_{P0}=1,2A$ for palladium acetate source and t=8 minutes for PVD deposition time. Alumina plates were used as substrates.





sample 1, d_{ss} =54mm



sample 2, d_{ss} =60mm



SDT MEASUREMENTS

All samples (1-3) were heated in argon and in the air atmosphere with the heating rate of 10°Cmin⁻¹ using SDT Q600 TA Instruments. Measurements in argon allow to determine the content of films's precursors (C_{60} and $Pd(OAc)_{2}$) in the initial materials, which did not completely decompose during PVD process. Concluding results of SDT method in the air atmosphere we can calculate Pd content in carbonaceous matrix assuming that all carbon was oxidized to CO_x (x=1or 2).



sample 3, d_{ss} =69mm

FTIR ANALYSIS



FTIR spectra of samples 1-3 confirm the presence of C_{60} and Pd(OAc)₂ in initial films what is consisted with SDT results. The broad bands at wavenumbers of 1590 and 1420cm⁻¹ attributed to asymmetric and symmetric stretching vibrations of C=O bond in carboxylate ion are ascribed to Pd(OAc)₂ molecules. The narrow band at wavenumber of 1183 cm⁻¹ is connected with C₆₀ pentagon asymmetric deformation. FTIR spectra show that the content of C_{60} and Pd(OAc)₂ in the initial films depends on the distance d_{ss} in PVD method. With increase of d_{ss} the intensity of characteristic bands decreases. Ratio of bands intensities found for C_{60} and $Pd(OAc)_2$ (In_{C60}/In_{Pd}) also decreases when this distance increases. Reasons of this are: 1) the thickness of films and 2) the concentration of

compounds, especially of C_{60} that can decrease in relation to $Pd(OAc)_2$ due to its high molecular weight.

Nr sample In_{C60}/In_{Pd(OAc)2} $(1183/1420 \text{ cm}^{-1})$





		(1100/14200111)	
	sample 1	0,47	
	sample 2	0,14	
	sample 3	0,13	
			_

		UI	

Nr sample	mass loss /	mass loss /	mass loss /	remnant/	remnant/	weight C ₆₀	
	Ar [%]	Ar [%]	Ar [%]	Ar [%]	Air [%]	weight Pd(OAc) ₂	
	100-300°C	300-500°C	500-880°C	950°C	950°C		
sample 1	11	5,6	34,1	47,4	14	1,7	
sample 2	19,9	6,2	14,8	56,4	16	0,4	
sample 3	18,6	7,2	5,1	67,3	29	0,15	
C ₆₀	-	-	<mark>86</mark>	10	0,06		
Pd(OAc) ₂	53,7			44,5 (600°C)	39,9		

This project is co-financed by the European Regional Development Fund within the Innovative Economy **Operational Programme 2007-2013 (title of the project "Development of technology for a new generation** of the hydrogen and hydrogen compounds sensor for applications in above normative conditions" No UDA-POIG.01.03.01-14-071/08-06)

> composition of initial films depends on distance between substrate and sources in PVD process. Pd content in PVD films increases with increasing the distance;

 \geq the increase of Pd content in carbon matrix is caused by a decrease in a weight ratio of C₆₀ to $Pd(OAc)_2;$

 \geq lower weight ratio of C₆₀/Pd(OAc)₂ in deposited film is probably due to C₆₀ higher molecular weight compared to the molecular weight of Pd(OAc)₂, thus less fullerene molecules reach the substrate placed in the larger distance from sources;

From SDT measurements performed in argon atmosphere we conclude that $Pd(OAc)_2$ in PVD films decomposes in the temperature range of 100-300°C, and C_{60} sublimates between 600 and 880°C

> from SDT measurements performed in the air atmosphere we can calculate Pd content in the initial PVD films



*

INNOVATIVE ECONOMY