Solid State Phenomena Vols. 203-204 (2013) pp 398-401

doi:10.4028/www.scientific.net/SSP.203-204.398

Changes in the Structure of Palladium Nanograins in the Carbon Film (C-nPd) under the Influence of Hydrogen

DIDUSZKO Ryszard [1,a], KOZŁOWSKI Mirosław [1,b], CZERWOSZ Elżbieta [1,c], KAMIŃSKA Anna [1,d], NIETUBYĆ Robert [2,e]

[1] Tele and Radio Research Institute, Ratuszowa 11 Str., 03-450 Warsaw, Poland

[2] National Centre for Nuclear Research, Sołtana 7 Str., 05-400 Otwock, Świerk, Poland

[a] rydidu@op.pl, [b] miroslaw.kozlowski@itr.org.pl, [c] elzbieta.czerwosz@itr.org.pl,

[d] anna.kaminska@itr.org.pl, [e] robert.nietubyc@ncbj.gov.pl

Keywords: palladium hydride, hydrogen sensor, GIXD, SEM.

Abstract. Carbonaceous – nanopalladium (C-nPd) films on insulating substrates, obtained by PVD (Physical Vapor Deposition) followed by the annealing method, are used for hydrogen sensors.

In this paper we present the results of XRD, SEM and electrical measurements of C-nPd films grown by PVD and then either annealed in an inert atmosphere or modified by CVD (Chemical Vapor Deposition). The structure of palladium grains were measured in a H_2/N_2 gas mixture atmosphere containing H_2 in the concentration range 0-4%. Our measurements showed that C-nPd films prepared by PVD and annealing method were flat and they consisted of sphere-like palladium nano-particles, uniformly distributed in the low-ordered carbon matrix. Effect of hydrogen partial pressure on the crystal structure was studied *in situ* in GIXD measurements, using a specially designed measuring holder cell. It was observed that at low partial pressure of hydrogen, palladium *fcc* metal particles transformed into solid solution Pd(H) (α-phase), which occurs in the *fcc* structure as well. Lattice constant of that solid solution increases with increasing hydrogen partial pressure in the gas atmosphere. After exceeding the critical value of the partial pressure of hydrogen, palladium transforms into the structure of palladium hydride PdH_x (β-phase), which has significantly larger lattice constant. This critical value of hydrogen partial pressure depends on the initial structure of C-nPd film, and consequently on the parameters of PVD process and annealing. This value usually corresponds to a few percent hydrogen content in gas mixture.

1. Introduction

The structure and the composition of carbonaceous – nano-palladium (C-nPd) films, that are new materials proposed for hydrogen sensors or hydrogen storage, affect their sensing or storing properties. This type of materials can appear in the various structural forms of both components: palladium and carbon matrix. Nano-palladium can be found in the form of nano-particles, nano-wires or nano-crystallites, whereas the carbon matrix can be porous, amorphous carbon or higher ordered nanostructures. The structure of palladium is of a great importance for hydrogen sensing properties of C-nPd films. Bulk palladium is of the *fcc* structure, with the lattice constant $a = 0.3890$ nm. Palladium nano-clusters occur in icosahedral, decahedral or *fcc* forms, depending on the cluster diameter. The size regime for cluster stability computed by molecular dynamics and presented in [1].

Depending on an amount of hydrogen absorbed into palladium nano-clusters the formation of two main phases, α and β, of *fcc* palladium hydrides are observed [2]. The α-phase, which has the lattice constant close to that of bulk palladium ($a \cong 0.3890$ nm), occurs at the lower hydrogen concentrations, approximately $PdH_{0.15}$. This phase transforms into the β-phase having the stoichiometry PdH_x, $0.6<x<0.8$, and the lattice constant of approximately $a \cong 0.4020$ nm, at the higher hydrogen content which depends on a temperature and a pressure of surrounding atmosphere [3].