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Influence of hydrogen on the properties of nanostructured C-Pd films for sensing applications

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In this paper we present the results of the investigations of nanostructured C-Pd films for hydrogen sensing applications. These C-Pd films were prepared by physical vapor deposition and then annealed in an argon flow at the temperature of 500°C. The structure and morphology of the prepared C-Pd films were investigated using transmission electron microscopy and energy dispersive X-ray spectroscopy. We studied the influence of hydrogen on the electrical properties and crystal structure of C-Pd films. It was shown that film resistance changes depended on hydrogen concentration. At lower hydrogen concentration (up to 2 vol.%), the films response increased proportionally to [H_2], while above 2 vol.% H_2, it was almost constant. This is connected with the formation of a solid solution of hydrogen in palladium at lower H_2 concentration and the creation of palladium hydride at higher H_2 concentration. X-ray diffraction was used to confirm the formation of Pd-H solid solution and palladium hydride.

Keywords: C-Pd films, hydrogen sensor, GIXD measurements, resistance changes.

INTRODUCTION

Hydrogen gas is considered to be one of the most promising clean energy carriers for use in fuel cells due to its efficiency and environmental friendliness.[1] Hydrogen has also been widely used for conventional technology such as hydrocracking of paraffin hydrocarbons in petroleum refineries and many hydrogenation/dehydrogenation industrial processes[2–4]. The development and expanded use of hydrogen gas as an energy carrier and as a chemical reactant has caused an increasing demand for fast, sensitive and accurate hydrogen sensors. This is connected with the high flammability and explosiveness of hydrogen as well as a high leaking tendency because of its small molecular size[5]. One of the most thoroughly studied hydrogen sensors are palladium-based devices[6–9]. This is associated with the highly selective interaction between palladium and hydrogen, which results in changes in palladium electrical properties[6, 10]. The interaction of hydrogen with palladium begins with the adsorption of molecular hydrogen on palladium surface[11]. Then the palladium atoms catalyze the homolytic dissociation of H_2 to hydrogen atoms. These hydrogen atoms diffuse into Pd lattice and occupy its interstitial sites, forming a solid solution[1, 6]. The resulting solid solution of hydrogen in palladium has higher resistance compared to metallic palladium[11]. If the hydrogen partial pressure in the gas phase exceeds 1 kPa–2 kPa, the further incorporation of hydrogen atoms induces a phase transition from the α- to β-phase and the creation of palladium hydride (PdH_x)[12, 13]. This leads to an increase of the lattice constant, and thus the diameter of the palladium nanograins also increases[14, 15].

In this paper, we studied changes in the electrical properties and the crystal structure of carbonaceous-palladium (C-Pd) nanocomposite films under the influence of hydrogen. These C-Pd films were prepared by physical vapor deposition (PVD) and then annealed in an inert gas flow at a temperature of 500°C. Such films contain palladium nanograins embedded in the carbonaceous matrix. The carbonaceous matrix stabilizes palladium nanograins in C-Pd films, while Pd nanograins react with hydrogen, which leads to changes in the film electrical properties and structure. The structural changes occurring during hydrogen absorption were studied *in situ* using the X-ray diffraction method. Hydrogen sensing measurements in the H_2/N_2 mixture were performed to determine the films sensitivity and response time. We have correlated changes in C-Pd film sensitivity and response time toward various hydrogen concentrations with the changes in the film structure.

EXPERIMENTAL DETAILS

Nanostructured carbonaceous-palladium (C-Pd) films were prepared by physical vapor deposition (PVD) and then annealed under an argon atmosphere. In the PVD process the films were deposited on unpolished fused silica substrates, using two separate sources containing fullerene C_{60} (Sigma-Aldrich, 99.9%) and palladium acetate (Sigma-Aldrich, 99.98%)[16]. The resulting films were annealed at a temperature of 500°C in an argon flow rate of 40 L/h. Depending on the technological parameters of the preparation, films with a different structure, palladium content and electrical properties were obtained. The structure of the prepared films, palladium content and distribution of the palladium nanograins were studied using a Titan 80–300 Cubed transmission electron microscope (TEM) operating at 300 keV incident electron beam energy, equipped with an energy dispersive X-ray spectroscope (EDS). The specimens were prepared by the mechanical stripping of the C-Pd films on a 1.000 mesh grid.

X-ray diffraction studies were carried out on the W1 beamline at Doris III synchrotron at Hasylab. GIXD (Grazing Incidence X-ray Diffraction) measurement geometry was applied due to the low thickness (up to 300 nm) and low absorption of the C-Pd films. A double Si (111) crystal monochromator provided radiation with a wavelength of l = 0.154056 nm, equal to that of the $K_{\alpha1}Cu$ fluorescence line, was used. The effect of the hydrogen partial pressure on the crystal structure was studied *in situ* in GIXD measurements with the 2° inci-