Influence of PdH$_x$ formation ability on hydrogen sensing properties of palladium-carbonaceous films[☆]

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ABSTRACT

In this paper we present new nanocomposite materials ability to use in hydrogen sensing applications. Nanocomposite films were obtained by several techniques such as PVD, PVD/CVD (physical vapor deposition/chemical vapor deposition) methods as well as by annealing of films prepared by PVD process. The films are composed of Pd nanograins embedded in the carbonaceous matrix. These Pd nanograins are responsible for palladium hydride PdH$_x$ formation. Creation of PdH$_x$ in these films was observed during in situ GIXD (graizing incidence X-ray diffraction) measurements. The hydrogen sensing characteristics by dc electrical measurements were also shown. We discuss how the structure of Pd-C films, palladium nanograins and the carbon matrix affect the sensing properties in terms of response time, sensitivity and reversibility.

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1. Introduction

Hydrogen (H$_2$) is widely used in industrial applications such as the preparation of ammonia (NH$_3$), hydrogen chloride (HCl), and methanol (CH$_4$OH), hydrogenation of organic compounds and in the production of semiconductors, petroleum recovery and refining, and it is used in fuel cells to power consumer electronic devices. Fuel cells are currently used in vehicles and power generators and are the electrochemical devices that convert directly chemical energy into electrical energy. Hydrogen is also applied in the reduction processes (e.g. metals oxides) and in hydrogenation (solidification) vegetable oils in the food industry. Due to its physico-chemical properties such as low mass density, light weight, odorless, colorless and high explosiveness when it is mixed with air at a minimum ratio of 4 vol.% [1], the installations, gasholders in which hydrogen gas is used must be monitored to prevent uncontrolled leakage of this gas.

Currently many type of solid-state H$_2$ sensors can be easily interfaced with the process stream, for example SAW (Surface Acoustic Wave) devices [2], metal-oxide-semiconductor (MOS) sensors [3] or devices such as metal-oxide-semiconductor field-effect transistors (MOSFETs). Some of these sensors are based on transition metals (e.g. nickel, palladium, platinum or its alloys) because solubility of hydrogen gas in these metals is very high [4]. Adsorption of H$_2$ changes the physical, electrical and optical properties of transition metals and their alloys therefore it can form the basis of operation of hydrogen gas sensors [5,6].

Palladium (Pd) is an ideal material for hydrogen sensing because at room temperature and atmospheric pressure it selectively absorbs hydrogen gas and forms a chemical species known as a palladium hydride (PdH$_x$) [7]. Hydrogen adsorbing on Pd surface is dissociated into atoms which diffuse into the octahedral interstitials sites of Pd *fcc* structure and elongate the Pd–Pd interatomic distance [8]. Depending on the amount of absorbed hydrogen two different *fcc* phases of PdH$_x$ can be formed [1]. At low H$_2$ concentration ($x < 0.02$) hydrogen with Pd forms solid-solution phase called the α phase. In this phase hydrogen atoms occupy randomly the octahedral interstitials and cause an insignificant increase of *fcc* lattice constant of about 0.15%. When x is between 0.02 and 0.6 the second phase called the β phase (metallic phase) appears and coexists with the phase α together. At concentration greater than $x > 0.61$ the phase α disappears and only the phase β remains. The lattice expansion in the β phase is larger and equals about 3.4% [9]. It is known that between these two phases there is a significant boundary in the bulk Pd, but in nanostructural forms of Pd (e.g. nanoparticles [10], nanotubes [11], nanowires [12]) these differences are much smaller.

Generally the H$_2$-sensing performance of the Pd nanostructures is better than that of bulk Pd, due to the high surface-to-volume ratio. It causes that low-dimensional Pd nanostructures are so

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