Nanocomposite carbonaceous-palladium thin films for ammonia sensors

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Abstract. Nanostructural carbonaceous-palladium (C-Pd) films for ammonia sensing were studied. These C-Pd films were prepared in a two-step process: the first one involved physical vacuum deposition (PVD) and the second one chemical vacuum deposition (CVD). The structure and morphology of the obtained films were characterized with the use of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Measurements of ammonia sensing showed that resistivity of the film changes with ammonia content in ambient atmosphere.

1. Introduction

Ammonia is one of the most common chemicals. Due to its high nitrogen content, ammonia is mainly used as a fertilizer. Ammonia also finds its industrial applications, e.g. in cleaning, refrigeration engineering, manufacturing of various chemical products, textile, and finishing. Although ammonia is so widely used it is both caustic and hazardous because of high toxicity. Ammonia gas is dangerous and harmful. Its detection makes an important issue.

There are a lot of sensors for ammonia [1], most of them based on zinc oxide as the active material [2-5] or on titanium oxide [6,7]. They have high power consumption since proper operation of sensors requires the use of heating elements. Ammonia gas is very corrosive, often resulting in a drift and short life of the sensors.

In this paper we propose to apply nanocomposite carbonaceous-palladium films for ammonia sensing. Based on our previous studies [8-11] we know that these films have a highly-developed surface and they are porous.

Specially manufactured carbonaceous-palladium films are sensitive to ammonia and do not require heating. They also demonstrate promising sensory properties for the detection of ammonia. The cost of producing a sensor based on carbonaceous-palladium films and materials for the sensors is low.

The ammonia sensing mechanism could depend on a change in the concentration of charge carriers in the C-Pd films [12,13]. Such an explanation was proposed for palladium/polypyrrole nanocomposite films [14]. Chemisorption of ammonia molecules on the surface of palladium nanograins is accompanied by a charge transfer from NH₃ to Pd, leading to the reduction in the
number of holes in the studied films. This causes a change in the film electrical properties. However, a different reaction could take place in the case of C-Pd films. Brown [15] and Allen, Goddard & Schaefer [16] suggested and calculated that the ion-molecule reaction between C+ and NH3 might produce a significant amount of H2NC+ ion in addition to the linear HCNH ion as well as H atoms; namely,

\[ \text{C}^+ + \text{NH}_3 \rightarrow \text{H}_2\text{NC}^+ + \text{H} \]

the metastable H2NC+ ion can then undergo a dissociative recombination reaction with electrons which, unless there is a considerable rearrangement of the atoms, produces only HNC as well as hydrogen atoms:

\[ \text{H}_2\text{NC}^+ + e^{-} \rightarrow \text{HCN} + \text{H} \]

These hydrogen atoms could penetrate into palladium crystals. The electrical properties of the entire C-Pd film could also change due to both effects.

In this work we present the results of studies on the interaction between ammonia and C-Pd films. We found that the resistance of C-Pd films is increasing in the presence of ammonia gas. We also found that the structure, topography and morphology of the film strongly depends on the temperature of the CVD process.

2. Experimental

The C-Pd films were obtained in a two-step PVD/CVD process that is described in papers [17, 18]. We used fullerene C_{60} (Sigma-Aldrich, 99.9%) and palladium acetate (Sigma-Aldrich, 99.98%) as the film precursors in the PVD process. The same technological parameters were used in all PVD process to prepare samples. The films were deposited on alundum (Al_{2}O_{3}) substrate.

The C-Pd PVD films were modified in the second step, in which the pyrolysis of xylene (C_{8}H_{10}), as the source of carbon, proceeded. The pyrolysis temperature 550°C for sample P1, 650°C for sample P2 and 750 °C for sample P3. The xylene flow and duration of the CVD process were the same for all applied temperatures.

Scanning Electron Microscopy (SEM) and TEM were used to characterize the structure and morphology of the obtained films. SEM examination was carried out with the JEOL JSM-7600F field emission scanning electron microscope operating at 2keV and 5keV incident energy. The structure of the films annealed at 550°C, 650°C and 750°C was investigated with Scanning Electron Microscopy (SEM) in a dual imaging mode: SE (Secondary Electron) imaging and LABE (Low Angle Backscattering Electron) imaging.

TEM investigations were carried out with Titan 80-300 Cubed transmission electron microscope (TEM) operating at 300 keV incident electron beam energy.

A special measurement chamber was used to measure the sensitivity of films for ammonia. The measurement chamber had an electrical feedthrough, gas flow inlet and outlet. The gas flow inlet was driven by a mass flow controller. The flow of NH_{3}/N_{2} mixture (100 ppm NH_{3}) was set at the level of 50 ml/min. Measurements were carried out at a room temperature and under atmospheric pressure. The desorption of ammonia was performed in the airflow. Electrical resistance of C-Pd films was measured during their interaction with ammonia. Contacts for resistance measurements were obtained by applying conductive silver paint (SPI Supplies) to the films.
3. Results and discussion

3.1. SEM characterization

The structure of films that were obtained in the PVD process varies depending on the sample position in relation to the sources of palladium acetate and fullerene. SEM images show that the films are composed of grains with different shapes and diameters, arranged layer by layer on the substrate. The structure of the film suggests that grains grow in a form of independent islands. These islands are in a form of large 200 nm grains (Figures 1a, 2a, 3a). The film topography changes due to the surface filling with the islands.

The structure of films modified with CVD changes with the annealing temperature. Pd nanograins in the C-Pd layer agglomerate due to annealing. For C-Pd films obtained at 550°C and 650°C the effect of Pd nanograins agglomeration can be observed (Figures 1b and 1c, Figures 2b and 2c). The newly formed grains are shown as bright objects in a SEM image in the LABE mode (Figures 1c and 2c). These Pd grains have a diameter of a few hundreds nm. On the surface of the film modified at 550°C and 650°C we observe many randomly distributed islands of a porous carbonaceous structure (Figures 1d and 2d) and small Pd grains (Figures 1c and 2c). Such superficial Pd grains can be seen as bright objects in Figure 1c and 2c. For C-Pd film modified by CVD at 550°C we observe that the carbonaceous islands are coated with Pd nanograins (Figure 1d).

Smaller Pd grains are observed for a film annealed at 750°C (Figure 3b, c). These Pd grains are situated on the edges of the substrate huge grains (> a few micrometers). On the flat fragments of the film surface, Pd nanoparticles with a diameter of ca. 1 micron are clearly visible at high magnification (Figure 4a, 4b). Besides these large grains, a lot of very fine Pd nanograins are found on the film surface. These nanograins are densely and uniformly distributed on the surface.

Fig. 1. SEM images of sample P1 surface a) after PVD process, b) after CVD process (temp. 550°C) SE imaging, c) after CVD process (temp. 550°C) LABE imaging, d) SE imaging of a fragment of a carbonaceous island coated with Pd nanograins

Fig. 2. SEM images of sample P2 surface a) after PVD process, b) after CVD process (temp. 650°C) SE imaging, c) after CVD process (temp. 650°C) LABE imaging, d) SE imaging at 100,000 magnification, showing a porous island
Fig. 3. Images of SEM of sample P3 surface a) after PVD process, b) after CVD process (temp. 750°C) SE imaging, c) after CVD process (temp. 750°C) LABE imaging

Fig. 4. Images of SEM of sample P3 surface a) after CVD process (temp. 750°C) SE imaging, b) after CVD process (temp. 750°C) LABE imaging

TEM images of the annealed films are presented in Figures 5a, b and c. For the C-Pd film modified at 550°C only small Pd nanograins (5-10nm) with fcc structure type are observed. The structure of the Pd grains was determined based on the analysis of the electron diffraction pattern. A higher temperature of CVD process causes a formation of larger Pd grains, with sizes significantly exceeding 200 nm for 650°C and with sizes up to 150 nm for films obtained at 750°C. It should be noticed that Pd nanograins, observed in films obtained at 750°C, are surrounded with a carbon shell. It shows in Fig. 5c, where the dark objects are Pd nanograins and a lighter shell can be seen around each Pd nanograin.

Fig. 5. Images of TEM of C-Pd films obtained at: a) 550°C, b) 650°C and c) 750°C. The circle in Figure 5c marks the area with Pd nanograins surrounded with carbon shells. The insert presents the electron diffraction pattern for relevant films.
3.2. Sensing Measurements

The sensing measurements for annealed C-Pd films are based on changes in the film resistivity in ambient atmosphere containing ammonia. These changes are analysed according to the following formula:

\[
\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \times 100\%
\]

where \( R \) stands for the sample resistance in the test gas and \( R_0 \) stands for the sample resistance in the air.

The resistivity of the films increased after introducing ammonia to the measurement chamber, while the initial resistivity of these film was \( 2.5 \times 10^3 \, \Omega \cdot \text{m} \). Such resistivity value could be attributed to the presence of many porous carbon islands. Kennedy et al. [19] studied resistivity of such materials and they found that this resistivity was \( 10^2 - 10^3 \, \Omega \cdot \text{m} \).

Introduction of air into the measuring chamber causes a decrease in resistivity of samples but did not restore the initial resistivity value. Figures 6a, b and c present the results obtained for the three investigated samples P1, P2 and P3 respectively.

Fig. 6. Sensitivity of C-Pd films versus time of exposure to 100 ppm NH\(_3\): a - sample P1, b - sample P2, c - sample P3.

It should be noticed that P1 demonstrated the best response for ammonia, while P2 revealed the worst one. Taking into account the mechanism of electrical change of the C-Pd film during an interaction with ammonia suggested in the introduction, we can suppose that the presence of a porous carbonaceous structure, rich in C\(^+\) ions is the most important factor in the process of ammonia decomposition and hydrogen incorporation into palladium grains. This leads to a formation of PdH\(_x\) whose resistivity is higher than the resistivity of palladium. Consequently, the film resistivity during ammonia absorption increases.

4. Conclusions

Nanocomposite carbonaceous-palladium (C-Pd) films, prepared at the Tele and Radio Research Institute, make promising materials for ammonia sensor applications. The films were characterized with SEM (after PVD and PVD/CVD process). Ammonia sensing properties were also measured for all these films. Our SEM investigation of the initial film obtained from the PVD process reflected the substrate surface shape, which is composed of angular grains of few hundreds nm in size. Microscopic studies of the PVD/CVD films revealed that the film topography and morphology strongly depends on...
the temperature of CVD process. The best sensing properties were obtained for films where Pd nanograins formed conducting paths on the edge of large grains of a substrate covered with C-Pd film and many porous carbon islands were located on the film surface. The worst sensing properties were observed for a film without such conducting paths. In the film annealed at 750°C, Pd nanograins were surrounded with carbon shells that impeded hydrogen desorption.

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