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Solvothermal synthesis of highly dispersed Pd-decorated ZnO with high sensitivity to acetone

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Summary:
The present work describes a relatively simple and easily scalable synthesis procedure of highly dispersed zinc oxide decorated with nanoscale palladium. The nanopowder has been characterised using a number of physical and chemical analytical techniques (DSC/TGA, XRD, SEM, TEM, XPS, EDX). The glass-ceramic MEMS-type microhotplate fabricated by screen-printing process was used for the deposition of the sensing layer. It is shown that the nanomaterial based on palladium-decorated zinc oxide shows a high response to ultra-low acetone concentrations.

Keywords: MOS-gas sensor, zinc oxide (ZnO), palladium (Pd), ceramic MEMS, acetone.

Introduction

Many international organizations, in particular the World Health Organization (WHO), Pan American Health Organization (PAHO), European Environment Agency (EEA) and the United Nations (UN), in their updated roadmaps further emphasize the need for various activities and research on public health (including primary and community healthcare (P&CHC) and environmental protection [1]. Due to this agenda, the requirements to environmental and biosphere monitoring devices are increasing significantly. The development of new relatively simple and easily scalable methods for the synthesis of basic MOS materials as well as methods for their modification is one of the most important tasks for the development of modern gas sensors as well as multisensor electronic nose technologies. On the other hand ,the application of "nano-on-micro" approach with nano-particle sensing material deposited on microfabricated hotplate is important trend in sensor development. Earlier in our research group, nanomaterials based on individual zinc oxide [2], including those decorated with platinum [3, 4], were obtained by the solvothermal method using various solvents.

Materials and Methods

The present work describes a relatively simple and easily scalable synthesis of highly dispersed zinc oxide decorated with nanoscale palladium. ZnO obtained by thermal degradation of zinc acetylacetonate hydrate in *n*-butanol [2] was used for the synthesis of ZnO-xPd nanocomposites (x=0.5 mol.%). Palladium (II) chloride $PdCl_2$ was used as a precursor of palladium nanoparticles. A pre-calculated amount of palladium (II) chloride was added to the dispersion of zinc oxide in ethylene glycol, and the dispersion was subjected to thermal treatment. The obtained powder after separation, drying and additional heat treatment was used to prepare a paste. The nanopowder was characterized using different physical and chemical analysis methods (DSC/TGA, XRD, SEM, TEM, XPS, EDX).

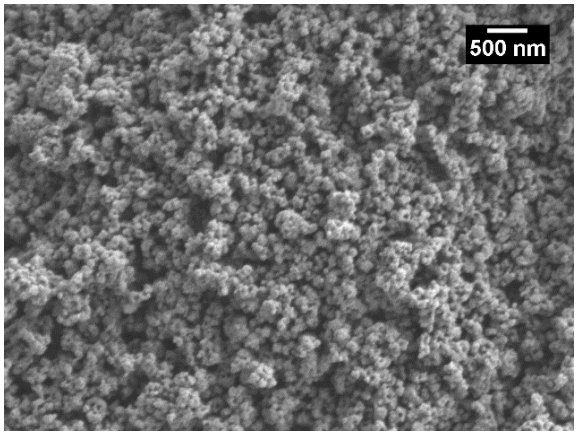

Fig. 1. SEM-micrograph of Pd-decorated ZnO powder

The sensing material was deposited onto the ceramic MEMS platforms using microextrusion printing system developed at the Institute of inorganic chemistry of RAS. The platforms were

cantilever-type structures made using screen-printing process with the application of sacrificial layer washable away after firing in a ultrasonic bath. The cantilever was equipped with microheater made of platinum composite material, the body of the microhotplate and isolation between microheater and sensing layer were made of composite containing alumina microparticles and SiO_2-B_2O_3-BaO-CaO-MgO-Al_2O_3 glass [5]. The electric leads to the sensing layer and to the microheater were made of platinum. The size of the chip was adjusted to the pin alignment of TO5 holder. The chip was fixed to the pins of TO5 with silver glue, which doesn't interact with other elements of the sensor at low temperature of the frame.

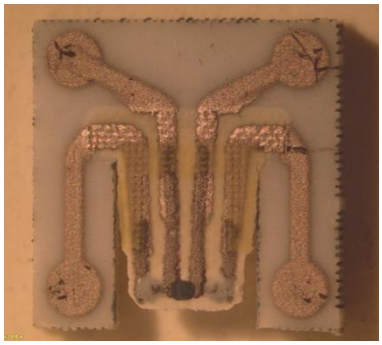

Fig. 2. Screen-printed cantilever type ceramic microhotplate with deposited sensing layer.

The cantilever type microhotplate with deposited sensing material is presented in Fig. 2. The microhotplate consumes approximately 120 mW of heating power at 450^{0}C.

Results

According to XRD data, ZnO powder has a crystalline structure of wurtzite phase (P63mc, PDF 01-070-8070). According to SEM data (Fig.1), ZnO consists mainly of nanoparticles with the size of 58±8 nm.

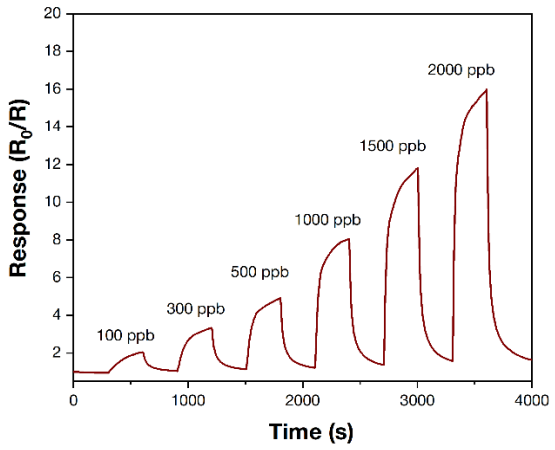

Fig. 3. Responses to 100-2000 ppb acetone at 300°C of Pd-decorated ZnO film

According to TEM data, Pd nanoparticles with an average size of 4±0.7 nm are located on the surface of ZnO. According to XPS data Pd is in oxidised state.

For the obtained ZnO-Pd film the gas-sensitive properties to a large number of analyte gases (CO, NH_3, NO_2, benzene (C_6H_6), acetone (C_3H_6O), ethanol (C_2H_5OH), H_2, methane (CH_4)) at 150-300°C were comprehensively studied.

It is shown that the highest response is observed when acetone is detected at 300°C. This temperature was tested and stabilized using pre-measured temperature coefficient of resistance (TCR) of the microheater. Fig.3 shows the responses (R/R_0) for 100-2000 ppb of acetone, which lie in a range from 2 to 16.

Thus, the obtained Pd-decorated ZnO nanomaterial shows high response to ultra-low acetone concentrations.

Acknowledgement

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