Improving the sensitivity of the ZnO gas sensor to dimethyl sulfide

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Abstract. This study was focused on how to improve the gas sensing properties of resistive gas sensors based on zinc oxide to dimethyl sulfide (DMS). The aim of this research was to investigate possible ways of improvement detection of dimethyl sulfide, such as volume doping with synthesized gold nanoparticles or applying sepiolite passive filter. The addition of noble metal into the gas sensing layer is a widely known method of increasing gas sensor response. Sepiolite is a clay mineral with highly porous structure consisting of nanotubes few micrometers long and water absorption abilities. In this work thick-film resistive gas sensors based on zinc oxide were made (pure ZnO, modified by gold nanoparticles, with the addition of filter) and tested for low concentration (2 ppm) of dimethyl sulfide. The sensitivities to DMS of developed sensors were compared. Attention was paid to the analysis of the impact of high humidity (90% RH) on the sensor time response.

1. Introduction
Gas detection is a common issue in environmental protection, work safety, automotive industry and alarm systems. Medical diagnostics is one of the more innovative application [1]. By detecting biomarkers, i.e. the compounds that are formed through metabolic processes in the body, we are able to notice potential disturbances in its functioning. More significant among such biomarkers, present in the exhaled air, are volatile sulfur compounds, such as dimethyl sulfide, whose increased concentration may indicate halitosis. It is a syndrome characterized by bad breath, which may be caused by liver or kidney disease, lung infection or the presence of undesirable bacteria in the mouth that cause damage to teeth and periodontal tissues [2, 3]. In order to detect small changes in concentration of dimethyl sulfide in exhaled air, a sensor sensitive to very low concentrations of this compound and resistant to the influence of high humidity is needed.

The most commonly used gas sensitive materials are metal oxides, such as zinc oxide, tin oxide and tungsten trioxide - semiconductors which, under the influence of particular gases, change their conductance. Among the most significant advantages are low production cost, high sensitivity, fast response time and the ability to detect different types of gases. Unfortunately, low selectivity is often mentioned as one of its disadvantages. In order to reduce these shortcomings filters [4] and dopants are used and the best operating temperature of sensor is matched up. The most popular gas sensitive layer dopants are metals such as gold [5, 6] and platinum [7].
In this paper the results of studies on chemical gas sensors implementation in halitosis detection are presented. The influence of dopants and filter on operating parameters of the sensors was examined. The study involved use of a thick film resistive gas sensor based on zinc oxide, material often used in detection of volatile sulfur compounds, carbon dioxide, acetone or ethanol, with high chemical and thermal stability. In order to improve sensitivity, synthesized gold nanoparticles were used as a dopant. Previous studies have shown that such additive, due to its high affinity for sulfur, significantly improves sensor sensitivity [8]. In result the lower detection threshold is decreased, which allows accurate measurement of e.g. dimethyl sulfide levels present in exhaled air. The nanometric dimensions of dopant guarantee its even distribution within the entire volume of gas sensitive layer and increases the active surface.

A great challenge during analysis of exhaled air is high humidity, above of 90% RH. It has a significant influence on sensors based on oxide materials, as adsorbed water molecules significantly impact conductance of the gas sensitive layer. To reduce distortions arising from presence of the water, a passive filter in form of sepiolite layer was used. Sepiolite is a clay mineral having a highly porous structure, consisting of nanotubes with a length of several micrometers. It is stable in the entire operating range of sensor [9] and has high adsorption capacity. Under the influence of temperature, various forms of water [10] are sequentially released from sepiolite: hygroscopic, zeolitic [11], molecules from nodes of octahedral structure and hydroxyl groups [12]. Preliminary studies have shown that presence of such filter significantly improves selectivity towards volatile organic compounds, rather than inorganic, and increases sensitivity. In this article methods of modifying sensor layer based on zinc oxide by gold nanoparticles dopant and sepiolite filter, in order to improve sensor sensitivity towards dimethyl sulfide, are presented.

2. Experimental part

2.1. Synthesis of materials

In preparation of the zinc oxide powders, commercially available reagents, characterized by the purity analytic grade 1M solution of zinc nitrate Zn(NO$_3$)$_2$ and a 1M solution of hexamethylenetetramine (HMT) were used. The solution was mixed in 1:1 proportion and then diluted to obtain concentration of 100 mM. Afterwards the solution was heated at 90°C for 8 hours. Resulting zinc oxide powder suspension was centrifuged, rinsed repeatedly with deionized water in the process of decantation and then dried using a lyophilizer.

Gold nanoparticles were prepared through reduction of chloroauric acid (HAuCl$_4$) by ascorbic acid. In reduction reaction of gold as stabilizers used low molecular weight polyethyleneimine (PEI) having an average molecular weight of 10 kDa, and Triton® X-100. In order to dope powder with gold nanoparticles, previously obtained ZnO powder was dispersed in isopropanol; then a solution of obtained gold nanoparticles with an average size of 17.5 nm was added to obtained mixture. The content of gold ions in solution based on weight of zinc oxide was 0.25% by weight. After stirring with a magnetic stirrer, solution was dried at 80°C and then heated in an oven at 450°C for 0.5 hours to remove organic residues.

Both pure and doped ZnO powders were processed into a paste was, which was screen printed onto alundum substrates. A series of sensors at different stages of modification was prepared:
- layer of zinc oxide;
- layer of zinc oxide doped with gold nanoparticles in an amount of 0.25 wt.%;
- layer of zinc oxide doped with gold nanoparticles in an amount of 0.25 wt.%. with a sepiolite filter.

2.2. Sensors preparation

Sensors were formed on an alundum ceramics substrate 250 μm thick. On one side of the substrate, a meander-shaped platinum heater and gold conductive paths (electric supplies to platinum meander) were printed. On the other side of the substrate, gold electrodes with gas sensing layer and a filter, each 40 μm thick, were printed (Fig. 1).
In paste preparation, an ESL-403 carrier manufactured by ESL Europe was used. The paste of given material was printed twice, with drying after each print, first at room temperature and second at 125°C for 10 mins. The complete structure of sensor was fired at 850°C for 2.5 hours. In the case of sensor with a sepiolite filter, the sensor layer was printed in such way that gas sensitive material had no direct contact with the atmosphere.

2.3. Electrical measurements
Sensor characterization was performed by a method known as Temperature Stimulated Conductance (TSC). The TSC method consists in measurements of sensor conductance as a temperature function. During measurements, tested sensor was placed in a chamber containing a gaseous atmosphere with a well-defined composition (synthetic air with humidity level at 30% RH or 90% RH and 2 ppm dimethyl sulfide). Working temperature of the heater was stimulated linearly with a constant increase of 2 deg/s in range from 150°C to 750°C (Fig. 2).

![Figure 1. A schematic cross-section of the sensor structure with a sepiolite filter.](image1)

![Figure 2. Schematic diagram of a measuring workstation.](image2)
Value of current flowing through the gas sensitive material was recorded during both growth and drop in temperature. Gas sensitive structure was polarized with a DC voltage, using Keithley 2400 current-voltage source and the electric current was measured. Then, using the Ohm's law, conductance of the gas-sensitive material was determined. Furthermore, sensitivity changes in function of temperature were determined; the sensitivity was defined as a ratio of sensor conductance in an atmosphere containing particular gas to conductance in synthetic air with humidity level at 30% RH. A sensor response, i.e. time until steadying of the output signal value after change from a steady value as a result of particular input signal ($\tau_{\text{resp90}}$) and recovery time ($\tau_{\text{rec90}}$), was also determined.

3. Results

The crystalline structure of obtained powders was determined by an X-ray Philips Materials Research Diffractometer equipped with a Cu Kα radiation source. Measurements were carried out by scanning the sample in an angle range $\Theta/2\Theta$. XRD studies have shown that the crystallographic structure of obtained oxide is the same as a model crystallographic structure of zinc oxide. The zinc oxide grains crystallized into a wurtzite-type structure with hexagonal unit cell and P63mc space group and lattice constants $a = 3.2501$ Å, $b = 3.2501$ Å and $c = 5.2071$ Å (Fig. 3).

![Figure 3](image)

**Figure 3.** An X-ray diffraction pattern of synthesized zinc oxide doped with gold nanoparticles.

A peak characteristic for gold was observed on diffraction pattern. However, due to a small weight quantity of dopant (0.25 wt.%) and its large dispersion in ZnO volume, this peak is not highly visible. The average crystallite size of ZnO was determined by Scherrer equation (1):

$$L_{(101)} = \frac{K \cdot \lambda}{B \cdot \cos \Theta}$$

where: $K$ – Scherrer constant (for ZnO was 0.9 based on [13]), $\theta$ – glancing angle a given interference band [rad]; $\lambda$ – length of an X-ray radiation beam [Å], $B$ – integral width (FWHM) of the peak (101) [rad].

As a result of an analysis of a diffraction peak corresponding to the plane (101) and based on the equation (1) the mean size of ZnO crystallites was 19 nm. Similarly, average size of gold crystallites was determined to approx. 5 nm.

Spectroscopic UV-vis measurements of colloidal gold solution were performed by Optizen $\alpha$-Hybrid Mecasys spectrophotometer. Quartz cuvettes were used during measurements. Absorption
spectra were recorded at room temperature and analyzed wavelength range was 200-700 nm. Analysis of colloidal gold sample showed a characteristic peak at a wavelength of 528 nm, which indicates presence of spherical gold nanoparticles (Fig. 4).

![UV-vis spectrum of obtained gold nanoparticles.](image)

**Figure 4.** UV-vis spectrum of obtained gold nanoparticles.

The size distribution of gold nanoparticles was determined by Dynamic Light Scattering (DLS). Tests were performed using a Nicomp 380ZLS (Particle Sizing Systems, USA) apparatus, equipped with a 50 mW laser operating at 532 nm wavelength. The average gold particle size determined by this method was approximately 17.5 nm (Fig. 5).

![Distribution of average size of gold nanoparticles carried out by DLS.](image)

**Figure 5.** Distribution of average size of gold nanoparticles carried out by DLS.

The substructure of gold nanoparticles and sepiolite was observed using EM900 Transmission Electron Microscope (TEM) (Zeiss, Germany). TEM analysis of nanoparticles revealed that obtained
nanoparticles have a spherical shape and sepiolite is composed of nanotubes having a length of several micrometers and a diameter of approx. 10-15 nm (Fig. 6).

In order to determine influence of gas sensing material, dopant and passive filter on sensor parameters during detection of dimethyl sulfide, electrical characterization of all three types of sensors was performed. Based on temperature stimulated conductance changes of sensor in humid dimethyl sulfide atmosphere, sensor sensitivity (Fig. 7) was determined. It has been found that use of dopant in form of gold nanoparticles significantly improved sensitivity towards examined sulfur compound. Furthermore, increase in sensitivity was observed after sepiolite filter was applied in addition to dopants. In this case the influence of water molecules desorption in whole temperature range is noticeable, which is a result of different water forms presence.

![Figure 6. TEM images of (a) gold nanoparticles; (b) sepiolite.](image)

![Figure 7. Sensor sensitivity in an atmosphere with a 2 ppm dimethyl sulfide and humidity of 90% RH.](image)

The response rate and recovery time of sensors were examined. These are important parameters of sensors, as they determine required measuring period and interval before next measurement (Fig. 8).
Figure 8. The response rate and recovery time of analyzed sensors after exposure to an atmosphere having a humidity of 90% RH containing 2 ppm dimethyl sulfide.

Noticeably, sensor based on pure zinc oxide has both longest response and recovery times. On the other hand, zinc oxide doped by gold nanoparticles responded fastest to presence of dimethyl sulfide. Presence of dopants not only improved sensitivity relative to determined gas, but also significantly affected pace increase. Additional presence of sepiolite is sort of barrier, extending adsorption and desorption of volatile compounds, which thus contributes to a slight increase in response and recovery times.

4. Summary

The article presents methods of modifying sensor layer based on zinc oxide by doping with gold nanoparticles and applying a sepiolite filter. Furthermore, effect of modifications on electrical characteristics of thick-layered resistive gas sensor during detection of dimethyl sulfide in atmosphere having a high humidity (90% RH) was determined.

All three sensors: based on pure ZnO, doped with gold nanoparticles and additionally coated with a sepiolite filter demonstrated good response relative to determined gas. Among analyzed sensors, ZnO+Au sensor was characterized by shortest response time (\( \tau_{\text{resp}90} = 26 \text{ sec.} \)) and by shortest recovery time.

The results show that with every further modification of sensor material and structure (filter presence), sensitivity to dimethyl sulfide is increased. Improvement of sensitivity by introducing gold nanoparticles in volume of gas sensitive material is due to high affinity of gold for sulfur compounds.

On the other hand, temperature stimulated changes in the structure of sepiolite and elimination of high humidity influence in analyzed atmosphere yielded a sensor with the highest sensitivity.

Further research will focus on increasing quantity of gas-sensitive layer dopants in order to determine best concentration, thereby to obtain maximum sensitivity relative to determined gas. It is necessary to perform further research in order to unravel in detail the mechanism of dimethyl sulfide oxidation on the surface of developed sensors.
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