

Au nanoelectrodes below nanostructured SnO₂ films for acetone detection during breath analysis

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Abstract:

New medical diagnostic methods such as non-invasive breath analysis bear the potential of drastically reducing medical costs as a greater amount of automatization is possible. Here, an asymmetric electrode assembly is described that increases the SnO₂ sensitivity and selectivity to acetone, a tracer for diabetes type-1, and reduces the resistance of the nanostructured SnO₂ layer. Gold nanoparticles serving as nanoelectrodes are stochastically deposited by flame spray pyrolysis (FSP) below a functional film decreasing the effective length of the resistive components. The feasibility of this assembly is demonstrated with solid state sensors having controlled resistance and exceptionally high sensitivity and selectivity to acetone. Au nanoparticles also enable detection of acetone at relatively low temperature with still high sensor response and signal to noise ratio.

Key words: nanoparticles, flame spray pyrolysis, breath analysis, gas sensor, Au, acetone.

Introduction

Breath analysis has the potential for detection and monitoring of several illnesses allowing a prompt medical treatment with higher chances of patient recovery, better quality of life and reduced medical costs. Furthermore, the prevention and treatment of organ failure or damage caused by oxidative [1] or metabolic stress [2] are critical issues during surgery. Early recognition of these pathological conditions by monitoring of specific breath markers offers the possibility to minimize organ damage [3].

Acetone is known to be an important breath marker for diabetes type-1, where its concentration changes from 300 to 900 ppb in healthy patients and to more than 1800 ppb for diabetics. A correlation between breath acetone and clinical/pathological condition has been shown to have potential for monitoring the state of the patients and timely initiation of life saving therapy [3].

Ethanol is another major component in the human breath, its average concentration is about 200 ppb [4], but, increases it dramatically when consuming alcoholic beverages. For instance, a concentration of about 80 ppm ethanol in the breath [5] is already reached at half (0.04 %) of the blood alcohol concentration (BAC), the U.S. driving limit today (0.08 %).

Fully integrated gas sensors made of nanoparticle films are a key technological development for advancing portability and performance of breath analysis methods [6]. SnO₂ is one of the most utilized and best understood prototype gas sensor [7]. It has high sensitivity to several analytes. Additionally, the integration of nanoparticles in sensors is a key technological development for advancing their performance, miniaturization and reduction in power consumption. Frequently, however, the benefit of nanoscale is lost by poor electrical conductivity through such nanoparticle structures. Thus, it is challenging to achieve both miniaturization with maximal performance and attractive conductivity. Recently, it was suggested that a way out from the size/conductivity dilemma is the integration of two types of nanoparticles [8]. CuO nanoparticles utilized as nanoelectrodes decreased the SnO₂ films resistance up to 5 orders of magnitude [8]. Furthermore, addition of metal nanoparticles on semiconductor is a common way to enhance the sensor response. From previous studies Au, Pd, Pt and other metals have been applied to several semiconductor materials as dopants resulting in an increase of sensitivity or selectivity.

Here, we apply this approach to optimize the properties of gas sensors for selective acetone detection. To obtain the best performance, Au nanoparticles have been utilized as nanoelectrodes. Their size and the resulting film

thickness were correlated to the final performance establishing structural-functional correlations for several fundamental configurations.

Experimental

A flame spray pyrolysis (FSP) reactor was used in combination with a water-cooled substrate holder for synthesis and direct deposition of semiconducting SnO_2 and conductive Au nanoparticles films onto Al_2O_3 substrates featuring a set of interdigitated gold (macro) electrodes and a sensing area of 1 cm^2 . After deposition, the resulting films were mechanically stabilized by in situ annealing with a xylene-fed spray flame. The SnO_2 films were obtained by spraying and combusting tin (II)-ethylhexanoate (Aldrich, purity >98%) diluted in xylene with a total metal atom concentration of 0.5 M. Thin Au conductive layers were obtained by spraying 0.01 M hydrogen tetrachloraurate (III) hydrate (Sigma Aldrich) in xylene (Fluka, purity >98%). Flame settings are described in detail elsewhere [8].

Prior to sensing tests, the sensors were kept in an oven at $500\text{ }^\circ\text{C}$ for 5 hours at ambient pressure to thermally stabilize them and avoid nanoparticle sintering and thereby drift of the sensor signal during testing. The sensor measurements were performed as described more in detail elsewhere [9]. The sensor response (S) is defined as:

$$S = R_{\text{air}}/R_{\text{analyte}} - 1 \quad (1)$$

where R_{air} is the film resistance in air and R_{analyte} is the film resistance with a given concentration of acetone or ethanol.

Results and Discussion

Sensors based on SnO_2 showed sensitivity to several gases thus lacking of selectivity. Several materials, in particular metal oxides, have been used for detection of acetone in the past: TiO_2 , WO_3 , ZnO and many others showed promising results. Recently, it has been shown that decreasing the layer thickness of SnO_2 films increased the performance, increasing, however, the sensor resistance [8]. The sensor response to ethanol was increased by a factor 5 by decreasing the layer thickness from 600 to 50 nm and this was attributed to deeper penetration of analyte in thin rather than in thick films [8]. Here, SnO_2 films of about 200 nm have been deposited onto Al_2O_3 sensor substrates featuring gold interdigitated (macro) electrodes. These SnO_2 sensors showed comparable response to ethanol as in the literature [8] in the same thickness range: the present sensor response to 10 ppm ethanol was about 80 at

$320\text{ }^\circ\text{C}$ in dry air. Nevertheless, these sensors showed even higher response to acetone. For instance, the sensor response to 50 ppm acetone was more than 1500. As expected, the selectivity to acetone against ethanol, only a 2.5 factor, is not sufficient. This is because the acetone concentration in the human breath varies between 0 and 3 ppm [10] while the one of ethanol usually is approximately 200 ppb in average [4] but could reach up to more than 50 ppm after alcohol consumption.

Au nanoparticles were deposited on sensor substrate featuring gold (macro) electrodes (Figure 1). This discontinuous layer of nanoelectrodes consisted of an open circuit which is mandatory for sensor application to avoid the shunting of the film.

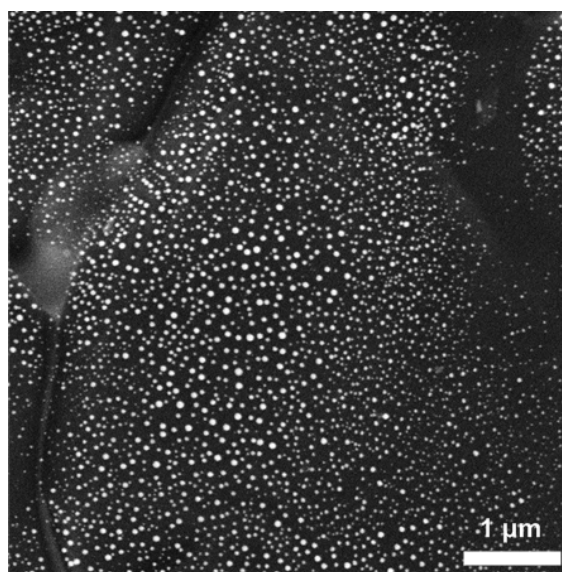


Fig. 1. SEM image of dispersed Au nanoparticles deposited on an alumina substrate. An open circuit layer of Au nanoelectrodes is visible on the Al_2O_3 substrate grains.

Figure 2 shows the enhancement in sensor response to acetone by adding Au nanoelectrodes below a SnO_2 functional layer at $320\text{ }^\circ\text{C}$. The sensor response is increased by more than a factor 2 by the presence of Au nanoelectrodes. Additionally, the ethanol sensor response with Au nanoelectrodes is decreased, by a factor 10, in comparison to that of pure SnO_2 sensors. Therefore, the Au nanoparticles promote the acetone sensor response, by enhancing the catalytic activity of SnO_2 while partially combusting ethanol decreasing its sensitivity. This seems to be one of the highest sensitivities and selectivities ever measured.

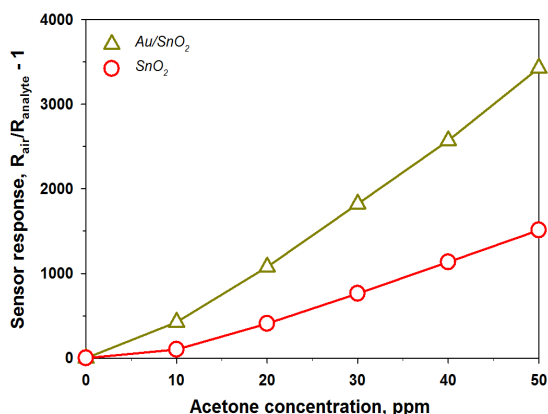


Fig. 2. Sensor response to different acetone concentrations of SnO₂ sensor (circles) and SnO₂ embedded with Au nanoelectrodes (triangles).

The sensing mechanism of these specific sensors is temperature dependent. Both the catalytic activity of the semiconductor surface and its electrical properties are strongly influenced by a change in temperature. Thus by placing catalytic active nanoparticles, such as Au, changes drastically the dynamics of the sensing mechanism. Thus the optimal operating temperature is dependent on the target analytes. Therefore, optimal operating temperature for these Au/SnO₂ sensors was investigated for the detection of acetone. Furthermore, the ability to detect low acetone concentrations (ppb) down to 140 °C has been demonstrated.

Conclusion

Au nanoparticles with controlled properties have been made and directly deposited by FSP onto sensor substrates and utilized as nanoelectrodes. This reduced the electric resistance of the functional SnO₂ film deposited above them resulting in an extremely high acetone sensitivity and selectivity over ethanol. Furthermore, it allowed the detection of ppb acetone concentrations at low sensor temperatures.

Acknowledgements

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