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Influence of Silsesquioxane-Containing Ultra-Thin Polymer Films on Metal Oxide Gas Sensor Performance for the Tunable Detection of Biomarkers

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Abstract: Certain biomarkers in exhaled breath are indicators of diseases in the human body. The non-invasive detection of such biomarkers in human breath increases the demand for simple and cost-effective gas sensors to replace state-of-the-art gas chromatography (GC) machines. The use of metal oxide (MOX) gas sensors based on thin-film structures solves the current limitations of breath detectors. However, the response at high humidity levels, i.e., in the case of exhaled human breath, significantly decreases the sensitivity of MOX sensors, making it difficult to detect small traces of biomarkers. We have introduced, in previous work, the concept of a hybrid gas sensor, in which thin-film-based MOX gas sensors are combined with an ultra-thin (20–30 nm) polymer top layer deposited by solvent-free initiated chemical vapor deposition (iCVD). The hydrophobic top layer enables sensor measurement in high-humidity conditions as well as the precise tuning of selectivity and sensitivity. In this paper, we present a way to increase the hydrogen (H_2) sensitivity of hybrid sensors through chemical modification of the polymer top layer. A poly(1,3,5,7-tetramethyl-tetravinylcyclotetrasiloxane) (PV4D4) thin film, already applied in one of our previous studies, is transformed into a silsesquioxane-containing top layer by a simple heating step. The transformation results in a significant increase in the gas response for H_2 ~709% at an operating temperature of 350 °C, which we investigate based on the underlying sensing mechanism. These results reveal new pathways in the biomedical application field for the analysis of exhaled breath, where H_2 indicates gastrointestinal diseases.

Keywords: sensors; tuning; hydrogen; PV4D4 polymer; silsesquioxane cage; functionalized; breath

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Citation: Lupan, O.; Brinza, M.; Piehl, J.; Ababii, N.; Magariu, N.; Zimoch, L.; Strunskus, T.; Pauporte, T.; Adelung, R.; Faupel, F.; et al. Influence of Silsesquioxane-Containing Ultra-Thin Polymer Films on Metal Oxide Gas Sensor Performance for the Tunable Detection of Biomarkers. *Chemosensors* **2024**, *12*, 76. https://doi.org/10.3390/chemosensors12050076

Received: 29 February 2024
Revised: 16 April 2024
Accepted: 29 April 2024
Published: 5 May 2024

1. Introduction

Certain molecules in exhaled breath are biomarkers and indicators of diseases. Recent analyses and studies have concluded that all humans generate a unique profile of volatile organic compounds (VOCs) in exhaled breath, which is a product of different metabolic activities in the human body [1–3]. Thus, any change in the VOC profile has the potential to confirm a particular disease. Consequently, their detection has attracted much interest in biomedical research. A non-invasive method is desired, allowing for a simple and cost-effective analysis of exhaled breath. As stated in various papers, at this time, non-invasive diagnostic methods such as gas chromatography/mass spectrometry (GC/MS) are considered to be the most accurate methods for obtaining a painlessly collected, extremely simple and non-invasive human breath sample [1,4].

However, this method faces many limitations due to its high cost requirements, including skilled technicians, the cost of GC/MS itself and the time required to analyze a sample. One approach to address these challenges is the development of metal oxide (MOX)-based gas sensors, which are capable of detecting low concentrations of various biomarkers/gases in human breath. More and more research studies are emerging in this direction. Recently, Lijuan Fu et al. reported a Co_3O_4/TiO_2 core–shell with high performance for the biomarker acetone [5]. In another study, Aasi et al. investigated atomically thin MoS_2 decorated with Pt or Pd as a promising material for colorectal cancer detection [6]. A recent review provides a comprehensive summary of the different biomarkers and the respective metal–organic frameworks applied for their detection [2]. One way to improve MOX sensors is to deposit different polymers on top of the sensors and anneal them at different temperatures to increase their properties, such as sensitivity and selectivity. A recent study presented a Cu-S semiconductor nanocomposite coated with a polyaniline nanocomposite applied for H_2S sensing [7]. As a result, it was concluded that the mechanism for improved sensing performance may be attributed to conductive composite networks. Another study obtained a Sb_2Te_3 sensor with polystyrene which resulted in good results for hydrogen sensing [8]. Some researches went further and demonstrated a wearable ethanol-sensing structure based on $Ti_3C_2T_x$ followed by functionalization using pyrrole on a disposable face mask [9]. In addition, it was demonstrated that different noble metals have an impact on different properties of TiO_2 based MOX sensors [10]. A recent review [11] mentioned that surface functionalization with different noble metal nanoparticles (NPs) improves different parameters, such as selectivity and sensitivity, as well as lowering the operation temperature and increasing long-term stability. Another recent study based on the structure-doping method [12], i.e., the use of Ag to dope an intrinsic graphdiyne with the purpose to detect SF_6 decomposition gas (HF, H_2S, SO_2, SOF_2, SO_2F_2), showed that the energy gap of the system was significantly decreased and the electrical conductivity was significantly improved after Ag doping. While mainly Ag and Pt seem to be used as catalysts for H_2 detection, there are also different studies that prove that there is no limit to the use of these metals for doping or functionalization with the purpose of enhancing different properties. For instance, Bi et al. [13] conducted a study on α-Fe_2O_3 functionalized with Ag-Pt. It showed a rapid response for triethylamine vapor sensing. Thus, a lot of practical trends can be explored. One of them is enoses. Enoses, usually made from an array of sensors [14], are intended to be used as odor detectors. Some researchers use noble-metal-sensitized SnO_2/RGO as enoses for H_2, H_2S and NO_2 [15], while others develop gas recognition models for the artificial olfactory system with gas sensor arrays [16]. In some reviews [17,18], the intention to use enoses is similar to the aim in this paper: they want to obtain a new method for non-invasive disease prediction based on different biomarkers. In some cases, even if good results are recorded, the sensor operation depends on temperature and therefore has to work at a higher operating temperature [19]. H_2, mainly because it is easily detected by MOX sensors, is a common target in this type of application and is being researched in the industry [10,20–27]. Furthermore, it is associated with different types of gastric diseases mentioned in [4] and described in more detail in a previous work [28]. Recently, it has also been associated with the possible up regulation of neurotransmitters involved in appetite stimulation, leading to hunger suppression and weight loss [29].

In this work, we present a new addition to hybrid gas sensors, which were reported in previous studies [4,10,30], to increase their response to H_2. A hybrid gas sensor consists of a MOX gas sensor coated with an ultrathin (~20–30 nm) polymer thin film on top of the sensor. This enables measurements in high humidity environments, which was always a problem related with conventional MOX gas sensors, as well as tuning of the sensor selectivity and performance [31,32]. High humidity levels are also encountered in exhaled breath. Hybrid sensors can circumvent this due to their hydrophobic character and enable the detection of biomarkers [6]. The polymer thin film is deposited via solvent-free initiated chemical vapor deposition (iCVD) [33]. This allows the conformal coating of complex MOX sensor structures with a polymer film, which can be tailored by deposition parameters and precursors. The basic reaction mechanism is free-radical polymerization. The transport of gas molecules through the polymer film is accompanied by the molecular characteristics and free volume in the layer. These results motivated us to further study the compatibility of hybrid sensors for biomarker detection in exhaled human breath to further tune selectivity. We investigate in this study the influence and transport of gas molecules through an ultra-thin polymer film containing silsesquioxane cage-like structures, which should provide a different free volume compared to the cyclotetrasiloxane rings in our previous study, using poly(1,3,5,7-tetramethyl-tetravinylcyclotetrasiloxane) (PV4D4) as the top layer. The silsesquioxane structures are obtained by the heat treatment of thin films of PV4D4 deposited by iCVD in oxygen, similar to the route reported by Trujillo et al. for the formation of low-k dielectrics [34].

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