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Detection of trace organophosphorus vapor with a self-assembled bilayer functionalized SiO_2 microcantilever piezoresistive sensor

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Abstract

Using piezoresistive SiO_2 microcantilever technology, we present an ultra-sensitive chemical sensor for trace organophosphorus vapor detection. A self-assembled composite layer of Cu^{2+}/11-mercaptoundecanoic acid is modified on the surface of the sensing cantilever as a specific coating to capture P═O containing compounds. Experimental results indicate that the sensor can be quite sensitive to DMMP vapor (well known as a simulant of nerve agent). The signal-noise-limited detection resolution of the sensor is experimentally obtained as low as several parts per billion. Besides that the sensor can yield reversible and repeatable response to DMMP vapor, adsorption of DMMP on the self-assembled composite layer is well fit to the Langmuir isotherm model.

Keywords: Microcantilever; Nerve agent; Trace chemical sensor; 11-Mercaptoundecanoic acid; Self-assembled monolayer

1. Introduction

Using chemical and biological warfare agents (CBWAs) as a measure of terrorism has become a real existing threat. The sarin attacks in the Tokyo subway in 1995 and the anthrax mailing incident in the USA in 2001 have increased the awareness of the public. Since the chemical warfare agents, especially the nerve agents, are highly toxic, early alarm and sensitive detection of these agents in trace level is of great importance. Accordingly, the study on detection of nerve agent has become a most active field, typically using dimethyl methylphosphonate (DMMP) as the simulant agent of sarin. All the time, researchers have been attempting to utilize a wide range of transducer technologies to meet these challenges, including electrochemical sensors [1–3], metal oxide semiconductor (MOS) devices [4–6], quartz-crystal microbalance (QCM) [7–9] and surface acoustic wave (SAW) technologies [10–15]. Based on the above-mentioned technologies, a variety of chemical sensors have been developed by coating a specific film on the sensitive structure. Despite that these sensors can provide a relatively quick and specific response to the nerve agents, there is still a critical need for more sensitive and accurate detection technology to fulfill the early alarm of the threats. Besides, many newly developed technologies and materials, such as fluorescence [16,17], metal–insulator–metal ensemble (MIME) chemiresistor [18] and microelectromechanical systems (MEMS) [19–28], are also utilized to make a more sensitive detection on the nerve agent in recent years. Among the above-mentioned technologies, the micromachined cantilever has been recognized as a unique and extremely sensitive platform for bio/chemical sensing [20]. The microcantilever-based sensors have many advantages, such as high sensitivity, fast response, low cost and on-chip integration. The micromechanical cantilever can be operated in two modes: static and dynamic. The microcantilever operating in a dynamic mode can translate specific mass adsorption into frequency shift. In contrast, the cantilever operating in static mode can yield an ultra-sensitive response to the specific adsorption induced surface stress. In 2003, Thundat and coworkers [21] reported a microcantilever-based sensing method for DMMP detection in aqueous solution, in which a self-assembled bilayer of Cu^{2+}/L-cysteine was

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used to specifically capture the organophosphorus compounds. Recently, the micromechanical cantilever sensor operating at dynamic mode was also utilized to detect organic vapors, where a thick film as sensitive coating is deposited at the sensitive spot on the cantilever. High sensitivity was achieved for detection of DMMP vapor [27]. In this paper, we present a novel SiO_2 microcantilever-based sensor operated in static mode. The measuring cantilever is functionalized with a self-assembled bilayer of Cu^{2+}/11-mercaptoundecanoic acid (11-MUA), which can specifically adsorb organophosphorus compounds *via* coordination. Response rate and sensitivity of the micromachined sensor to DMMP vapor are experimentally examined.

2. Experimental

2.1. Reagents and standards

The 11-mercaptoundecanoic acid was purchased from Aldrich Chemical Company with a purity over 95%. All other reagents were of analytical grade (A.R.) and were used without further purification. Deionized water (resistance higher than 18 MΩ cm) was used throughout. The reference gas of DMMP with a concentration of 1 ppm (5×10^{-3} mg L^{-1}) in nitrogen was supplied by Nanjing Mucop Nanfen Special Gas Co. Purity of the reference gas was examined to be over 99% by gas chromatography–mass spectroscopy (GC–MS).

2.2. Apparatus

MF-4 dynamic gas mixing apparatus was provided by Chinese National Research Center for Certified Reference Materials. Agilent-34401A multimeter was used to record the output voltage signal.

2.3. Fabrication of the cantilever-based sensor

The piezoresistive SiO_2 microcantilever is fabricated using standard micromachining techniques, with its schematic and dimensions shown in Fig. 1(a). The fabrication process begins on a silicon on insulator (SOI) wafer with p-type (1 0 0) Si top layer. Firstly, the top layer Si was thinned to a desired thickness and shaped to form piezoresistors after boron ion implantation. A thin oxide layer was formed by thermal oxidation and encapsulated the piezoresistors together with buried oxide layer of the SOI wafer. Then, the Al layer was deposited to form the electric connection. On the topside of the measurement cantilever, a 50 nm-thick gold layer on top of a 5 nm-thick chromium adhesion layer is deposited by electron beam evaporation. Finally, the Si below the buried oxide layer of the SOI wafer was etched to release the SiO_2 cantilever. Upon a surface stress induced by a specific reaction or binding [24,25], the SiO_2 cantilever will behave a much larger bending compared with the conventional Si or SiN_x cantilever, owing to the much lower Young's modulus of SiO_2. Therefore, this structure will lead to a more sensitive characteristic of the fabricated sensor. Moreover, the thin piezoresistors are fully covered by SiO_2, which features a much lower current leakage relative noise comparing to those

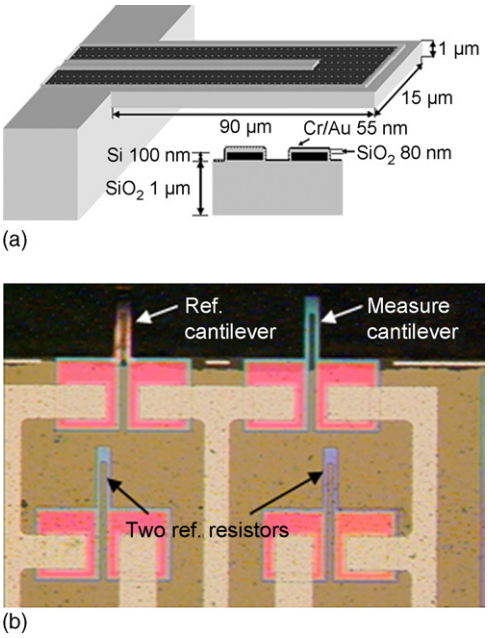

Fig. 1. (a) Schematic of the piezoresistive SiO_2 cantilever, with the dimensions and (b) top-view micrograph of the microcantilever sensor comprising a Wheatstone bridge for chemical sensing.

with p-n junction isolation. Therefore, the piezoresitive SiO_2 cantilever is expected to improve the noise-limited sensing resolution.

Fig. 1(b) shows the micrograph of the fabricated microcantilever sensor consisting of an on-chip integrated Wheatstone bridge, in which a piezoresistive cantilever is used for chemical measurement while another referential cantilever is used for canceling off the influence from environmental factors like temperature change, air flow, *etc*. For balance, two referential resistors are formed on the substrate and connected into the Wheatstone bridge. Such a sensing scheme has been approved with a remarkably reduced background drift and noise level [28,29]. The measurement cantilever can translate the surface stress induced cantilever bending stress into a piezoresistive output *via* the Wheatstone bridge. The piezoresistive sensitivity to surface stress of the cantilever is designed as $\sigma_s^{-1}\Delta R/R = 8.37 \times 10^{-4}$ m N^{-1}, where $\Delta R/R$ is the relative change of the piezoresistor. For the referential cantilever, there is no Au/Cr thin film on the piezoresistive cantilever surface. The cantilever will not be exerted with specific surface stress. It can only respond to environmental change for signal compensation.

2.4. Modification of the cantilever

For sensitive and specific detection of chemical vapors, a certain sensitive film should be modified on the measuring cantilever. In our experiments, we select a self-assembled bilayer of Cu^{2+}/11-MUA as a sensitive coating to capture organophosphorus molecules. This composite layer can specifically recognize P=O containing compounds with the formation of P=O–Cu^{2+} coordination structure on the surface. This sensitive coating has been demonstrated to be quite specific and sensitive to organophosphorus compounds [12,30,31]. Besides, it is found in