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RESEARCH PAPER

A Novel Porous Silicon Composite Sensor for Formaldehyde Detection

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Abstract: A novel palladium-porous silicon (Pd-PS) composite sensor was introduced for convenient and fast formaldehyde detection. Porous silicon was prepared by hydrothermal etching method and its surface micro-structure was characterized by scanning electron microscope. By optimizing the corrosion conditions of porous silicon, the optimum preparation conditions of porous silicon were obtained. In addition, palladium-porous silicon composite sensor was finally prepared by chemical immersion method to dope the metal palladium on the surface of porous silicon. When the prepared sensor was exposed to the mixed gas with formaldehyde, it exhibited a highly selectivity to formaldehyde molecules and could generate electrochemical signal that responded to the change of gas concentration. By detecting the electrical signal with a multimeter, the gas sensing properties of the sensor were investigated and discussed. The results indicated that the sensor was more sensitive to formaldehyde, exhibiting good selectivity. However, it was not sensitive to ethanol, ammonia, methanol and acetone. The detection rang of the sensor to formaldehyde concentration was 0.1–6.0 mg m^{-3}, with the detection limit of 0.1 mg m^{-3} and detection time of 3 min.

Key Words: Porous silicon preparation; Hydrothermal etching; Formaldehyde; Palladium-porous silicon; Gas sensor

1 Introduction

In recent years, with the improvement of living standard, people's demand for higher indoor environment quality has being growing. Formaldehyde from indoor decorating material is regarded as one of the most important indoor pollutants due to its highly toxic and potential carcinogenicity. WHO has classified formaldehyde as a potential carcinogen and one of the most important environmental pollutants. According to the *Hygienic standard for formaldehyde in indoor air of house* set by the People's Republic of China, the maximum allowable indoor concentration of the formaldehyde air is 60 ppb. While the threshold of formaldehyde concentration under indoor environment proposed by WHO is 74 ppb. However, the main detection methods for formaldehyde, such as the spectrophotometry and chromatography, have the shortcomings of high cost, long-time detection and impossibility of real-time online detection.

Porous silicon (PS) can easy to adsorb gas molecule due to its large specific surface area, which can effectively realize for gas detection. The detection principle of porous silicon gas sensor is mainly based on the changes of physical properties, such as the changes of electrical properties, the optical properties like photoluminescence (PL)[1], and the phenomena like fluorescence quenching or interference[2] caused by chemical absorption. However, PS is not stable, and is easily oxidized. Therefore, researchers tried a variety of metal nanoparticles film modification on the surface of PS. In 1993, Andsager *et al*[3] found that when porous silicon was immersed in Cu^{2+}, Ag^{+} or Au^{3+} solution, the fluorescence could be quenched; but when immersed in Ni^{2+} solution, the fluorescence was normal. Thus, they proposed the metal deposition on porous silicon for the first time. Wang *et al*[4] produced a heater formaldehyde gas sensor with nanometer SnO_2, and because of doping metal palladium, the sensitivity of the gas sensor was significantly improved. Deng *et al*[5]

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filled metal palladium on the surface of porous silicon by electro deposition method, and achieved better filling effect. In addition, according to the study conducted by Chen *et al*[6], the stability and luminous intensity of the porous silicon prepared through iron-passivated hydrothermal etching method were significantly improved.

After the intensive study on porous silicon, the application fields of porous silicon has been gradually widened and its sensitive materials have already been adopted in the detection of toxic gases[7], explosive substances[8], volatile organic compounds[9,10], DNA[11], and other proteins[12], etc. In addition, the nano-porous silicon materials became more and more prominent in the application field of optical detector, solar battery, lithium-ion battery and so on[13–15].

In this experiment, porous silicon was prepared by iron-passivated hydrothermal etching method. The porous silicon had smooth surface, same pore size, uniform distribution, and avoided the disadvantages of rough surface of porous silicon due to the uneven distribution of current by traditional electrochemical methods. After the surface of porous silicon was doped by metal palladium by chemical impregnation method, its sensitivity and selectivity to formaldehyde gas was significantly improved. By using a simple circuit, formaldehyde detection system examined the electrical signals by the digital multimeter. Thus it made the detection operation more convenient, and achieved real-time detection for formaldehyde. What's more, the sensor has many advantages such as convenient detection, low cost and high sensitivity.

2 Experimental

2.1 Instruments, materials and reagents

S-U1510 scanning electron microscope was from Hitachi Ltd. (Japan). ZK30BS vacuum drying oven was from Tianjin Sanshui Scientific Instrument Co., Ltd. (China). Ultrasonic cleaning equipment, FA2004A electronic analytical balance was purchased from Shanghai Jingtian Electronic Instrument Co., Led. (China). KH-100 mL hot water kettle was obtained from Beijing STWY equipment Co., Ltd.. Digital multimeter was used for the detection of electrical signals.

Silicon wafer used in the experiment was a kind of single crystal silicon of [100] crystal and p type (Tianjin Semiconductor Research Institute). The two types of resistivity of silicon wafer were 0.009 Ω cm and 0.1 Ω cm, respectively. Conductive silver glue was also used in the experiment.

Formaldehyde, ammonia, methanol, acetone, hydrofluoric acid, anhydrous ethanol, concentrated sulfuric acid (98%), hydrogen peroxide (30%), and potassium hydroxide were all the analytical reagents. Deionized water, palladium chloride, ferric nitrate and silver nitrate were also used in the experiment.

2.2 Pretreatment of silicon wafer

Before the start of the experiment, it needed to preprocess the silicon wafer by the following steps.

(1) Pieces: the silicon wafers were needed to be cut into 1.5 cm × 1.5 cm chips with glass knife.

(2) Cleaning: the silicon wafers were immersed in the mixed solution of 98% concentrated sulfuric acid and 30% H_2O_2 (3:1, *V*/*V*) until no bubbles were produced on the surface of silicon wafer. After being washed with deionized water, the silicon wafers were then immersed in the 20% HF solution (approximately 20 s) to remove the surface oxide layer. Finally, the silicon wafers were repeatedly washed with plenty of deionized water, and then were placed in anhydrous ethanol for ultrasonic cleaning about 25 min.

(3) Save: after dried, the cleaned silicon wafers were stored in the vacuum dryer or ethanol for the further use in the experiment.

2.3 Fabrication of porous silicon

In this study, hydrothermal etching method was employed to prepare porous silicon in the mixed etching solution of HF and $Fe(NO_3)_3$. In order to prevent the adverse effects of hydrogen bubbles in the corrosion process, a small amount of ethanol was added in the etching solution, and the filling coefficient was set to 0.7. Then the hot water kettle was placed in a vacuum drying box to receive hydrothermal treatment. The reaction temperature needed to be set. After a certain time of hydrothermal treatment, the hot water kettle was removed and had a natural cooling. After taken out, the samples were put in warm water, and washed with plenty of deionized water. Next, put the samples in the ethanol to get ultrasonic cleaning for 20 min. After washed by deionized water, the samples were naturally dried in a petri dish.

In order to obtain the excellent porous silicon, the preparation conditions were optimized, including the etching solution concentration ratio, the corrosion time, the corrosion temperature and the resistivity of silicon wafers.

Thereafter, the surface microstructure of porous silicon was observed by SEM, through which the optimal preparation conditions of porous silicon were determined.

2.4 Surface modification of porous silicon

By the electrochemical method, the metal palladium was doped on the surface of porous silicon. The electrolyte proportion was 5 mM HF and 0.5 mM $PdCl_2$. The electrolyte was added in the electrolytic cell with porous silicon as the cathode. After 30 s, porous silicon was removed, washed with plenty of deionized water, and dried naturally at room temperature. Thus, palladium-porous silicon (Pd-PS) composite element was prepared.