Applied Surface Science 268 (2013) 188–194

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Microstructure characterization and $NO_2$-sensing properties of porous silicon with intermediate pore size

Mingda Li, Ming Hu*, Qinglin Liu, Shuangyun Ma, Peng Sun

*School of Electronics and Information Engineering, Tianjin University, Tianjin 300072, PR China*

A R T I C L E   I N F O

*Article history:*
Received 1 September 2012
Received in revised form 8 December 2012
Accepted 11 December 2012
Available online 20 December 2012

*Keywords:*
Porous silicon
Electrochemical etching
Intermediate size pore
$NO_2$ detection
Room temperature

A B S T R A C T

In this work, a novel intermediate-size porous silicon (intermediate-PS) gas sensor was prepared successfully by electrochemical etching method. The morphology and geometry of PS samples were observed using field emission scanning electron microscope (FESEM). The surface chemical bonds were determined by Fourier transform infrared (FTIR) spectroscopy. It is found that PS showed typical n-type semiconductor behavior. Furthermore, it exhibited good response value, excellent repeatability and fast response–recovery characteristic when exposed to $NO_2$ gas at room temperature. Compared with other microstructures of PS, intermediate-PS showed much better gas-sensing properties because high special surface area provided more adsorption sites, and unique structural properties dramatically increased rates of gas diffusion. In addition, possible $NO_2$-sensing mechanisms and potential applications were also discussed.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

As a toxic, reddish brown and pungent odor gas, $NO_2$ is a major harmful pollutant in urban air, which resulted from combustion and industrial emissions [1]. Furthermore, $NO_2$ is a main source of acid rain and photochemical smog [2]. Therefore, $NO_2$ detection is important for both environmental protection and human health [3]. Unfortunately, there are few reports about a sensitive, stable and inexpensive gas sensor working at room temperature (RT) for $NO_2$ monitoring until now.

Porous silicon (PS) has been paid to extensive attention, which is one of the most important functional materials. PS could be used for solar cells [4], photonic [5], medical applications [6], and various types of sensors [7,8] because of huge special surface area and high surface chemical activity at RT [9]. What is more, PS can be potential compatibility with silicon integration technologies [10]. Many reports show PS-based gas sensor could be operated at RT [11,12], which is better than metal oxide-based semiconductor gas sensors [13].

Recently, PS gas sensor has been intensely investigated with $NO_2$ detection [14,15]. The gas sensing properties of PS strongly depend on porosity, pore diameter, uniformity as well as layer thickness [16]. Distinctive morphology and geometry of the pores can be obtained by adjusting electrochemical etching conditions, such as silicon type, electrolyte concentration, anodizing current density, etching time and illumination [17]. Although PS sensors show good sensitivity when exposed to $NO_2$, some problems such as selectivity, repeatability, response–recovery characteristics and long-term stability need to be considered. Some reports have been shown incomplete recovery, and irreversible changes restrict the PS for practical gas-sensing applications [18,19]. Actually, the PS with ordered pore channels may bring remarkable influences in the gas-sensing properties, including improved reversibility and response–recovery time.

There are several research efforts enabled to prepare PS with pore diameters in the range of a few nanometers to some tens of micrometers [20]. In general, according to IUPAC guidelines, PS has been classified depending on the pore sizes as micro-PS (<2 nm), meso-PS (2–50 nm) and macro-PS (>50 nm) [21]. The intermediate-PS (pore diameters 50–200 nm) has not been investigated intensively and systematically [22]. It is found that macro-PS with micron-sized pores could be open to the environment [23], which increased the gas diffusion significantly. However, the special surface area reduced markedly and then influenced the sensitivity of the gas sensor, compared with nano-sized meso-PS of branchy pore channels. As a result, the particular microstructure of intermediate-PS with higher special surface area than micron-sized macro-PS, and more gas diffusion channels than meso-PS. It can be concluded that the intermediate-PS could combine the advantages of meso-PS and macro-PS [24]. However, the intermediate-PS gas-sensing properties have not been studied so far.

Here, we comprehensively research the relationship between the microstructure of intermediate-PS and the $NO_2$ gas-sensing

* Corresponding author. Tel.: +86 22 87890662; fax: +86 22 27401233.
*E-mail address:* huming@tju.edu.cn (M. Hu).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.12.057

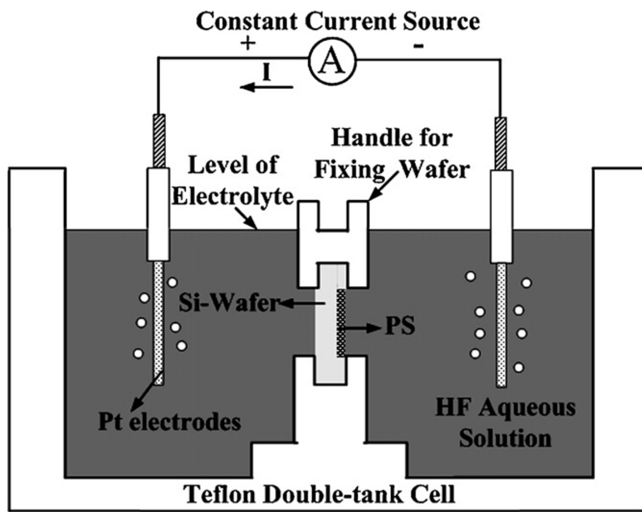


**Fig. 1.** Schematic diagram of electrochemical etching cell for preparing PS samples.

properties. These results could constitute a breakthrough in $NO_2$-sensing monitoring at RT.

## 2. Experimental

### 2.1. Porous silicon fabrication and structural characterization

Each PS gas sensor sample is 20 mm × 8 mm in size, fabricating on the polished surface of an n-type (1 0 0) monocrystalline silicon wafer with resistivity of 0.01 Ω cm. Firstly, all the samples were ultrasonically cleaned in deionized water, acetone and ethanol consecutively for 20 min each to remove grease and other possible pollutants from the surface. Then the samples were immersed in 5 wt.% HF aqueous solution for 10 min to remove the native oxide. After cleaned, the samples were rinsed in deionized water and then stored in ethanol to avoid surface oxidation for further use. The brown color anodization regimes were formed by using galvanostatic electrochemical etching method in a Teflon double-tank cell configuration. The silicon wafer was separated by two half-cells and platinum (Pt) electrodes were immersed in the electrolyte. The schematic diagram of the experiment setup is shown in Fig. 1. The whole etching process was carried out in the dark and at RT (25 ± 2 °C). The HF concentration in the electrolyte was 7.3 wt.% without any additional oxidizing agents. The applied anodization current density was kept at 125 mA/cm$^2$ by a constant current source (ATTEN, PCR70). Various PS samples were prepared by using different etching time ranging from 5 to 25 min. After anodization, all PS samples were thoroughly rinsed in deionized water and finally allowed to dry in ambient air.

Porosity is defined as the fraction of voids within the porous structure [25]. Measurements of the weight loss in the etching process were used as a gravimetric assessment to evaluate the PS porosity. The wafer was weighed using an electronic balance (LIBROR, AEG-120) with the least count of $10^{-4}$ g.

The following equations were used to obtain the average porosity percentage ($p$) and thickness ($d$) of the PS samples (Eqs. (1) and (2)) [26]:

$$p\,(\%) = \frac{m_1 - m_2}{m_1 - m_3} \tag{1}$$

$$d = \frac{m_1 - m_3}{\rho S} \tag{2}$$

The wafer was weighted before anodization ($m_1$), just after anodization ($m_2$), and after a rapid dissolution of the whole porous layer in the 1 wt.% KOH solution ($m_3$), respectively. Each sample was tested at least three times, and the average value was recorded. Where, $\rho$ is the density of silicon; $S$ is the etched area. Subsequently, the average porosity ($p$) and thickness ($d$) of each PS specimen was evaluated.

The plane and cross-section morphologies of PS samples were observed by field emission scanning electron microscopy (FESEM, FEI Nanosem 430; Hitachi S-4800 with an accelerating voltage at 10.0 keV and 5.0 keV, respectively). Plan-view micrographs showed the (1 0 0) plane, and the cross-section micrographs showed the pores in the (1 1 0) cleavage plane after cleaving the PS samples.

Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet Nexus 670 FTIR spectrometer) in the range of 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ for all analyses. It was utilized to determine the surface chemical species like Si—H and Si—O—Si bonds of intermediate-PS samples.

### 2.2. Preparation of porous silicon gas sensor

In order to fabricate PS gas sensor, two electrical contacts of platinum (Pt) thin films were deposited on the PS surface by RF magnetron sputtering. A DPS-III high vacuum facing-target magnetron sputtering system with a circular Pt target (2-inch diameter with 99.95% purity) was used for the deposition of films. The base vacuum pressure and working pressure were set at $4.0 \times 10^{-4}$ Pa and 2.0 Pa, respectively. Using the pure argon (Ar) as the sputtering gas in the RF power of 90 W ($I$ = 0.2 A, $U$ = 450 V) and the constant sputtering time was set at 8 min. The fabrication steps and device size of a resistance-based PS gas sensor is depicted in Fig. 2.

### 2.3. Gas sensor measurement system

The gas-sensing properties of PS samples were investigated according to the resistance measurement between two Pt electrodes by a homemade computer-controlled gas sensor measurement system as reported previously [27]. This system consists of a sealed 30 L polymethyl methacrylate (PMMA) test chamber, a data-acquisition PC and a UNI-T UT70D professional digital multimeter. The multimeter was used for continuously monitoring the resistance ($R$) change of PS sample. Each sample under test was placed on a plate fixed into the test chamber and made a good electrical connection with the multimeter by two test probes. The schematic diagram of the gas-sensing measurement

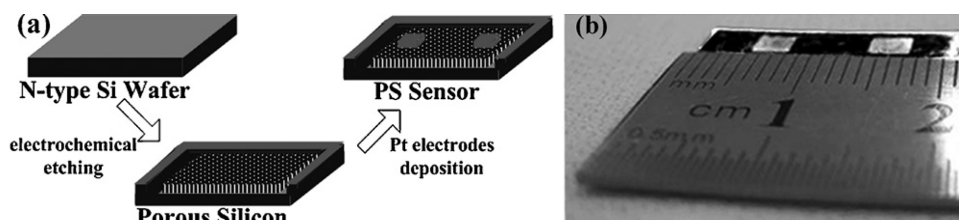


**Fig. 2.** (a) Schematic diagram of the fabrication steps of a resistance-based PS gas sensor; (b) the photograph shows the size of a resistance-based PS gas sensor.

Download English Version:

https://daneshyari.com/en/article/5360644

Download Persian Version:

https://daneshyari.com/article/5360644

Daneshyari.com