NO$_2$ sensing performance of p-type intermediate size porous silicon by a galvanostatic electrochemical etching method

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ABSTRACT

In this paper, a kind of novel p-type intermediate size porous silicon (Intermediate-PS) with large specific surface area and highly ordered pore channel was successfully prepared by a galvanostatic electrochemical etching method. The microstructure and surface bonding configuration of the PS characterized by using field emission scanning electron microscope (FESEM) and Fourier transform infrared spectroscopy (FTIR), respectively. The freshly prepared PS could achieve stable surface passivation after one week storage in air due to the effect of natural oxidation. Moreover, the NO$_2$ gas-sensing performances of the PS sensor were systematically investigated at different temperatures ranging from room temperature (25 °C) to 100 °C over NO$_2$ concentrations in the range of 0.125–2 ppm. The gas sensor based on the Intermediate-PS showed a typical p-type semiconductor behavior together with perfect reproducibility and very rapid response–recovery speed at room temperature. The good sensing properties of the Intermediate-PS sensor can be attributed to its favorable microstructure features. In addition, the conceivable sensing mechanism has also been discussed in detail.

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1. Introduction

Over the past few decades, with the rapid development of industrialization, air pollution problems have become more and more serious and can cause harmful effects to human health. As a typical air pollutant causing photochemical smog and acid rain, nitrogen dioxide (NO$_2$) is very dangerous to the environment protection [1,2]. Simultaneously, NO$_2$ pollution has a very bad effect on the human's lung function and respiratory system even in low concentrations (3 ppm or more) [3]. For environmental protection and human safety, the development of NO$_2$ gas sensor has been urgently expected in domestic and industrial areas. At present, NO$_2$ gas sensors based on various semiconducting metal oxides (e.g. ZnO [4], SnO$_2$ [5], WO$_3$ [6]) have been widely investigated. However, in order to achieve excellent sensing performances, metal oxide based sensors usually need to operate at high temperatures (>100 °C), which require to attach heating elements for supplying thermal energy. Such inherent drawback increases power consumption and reduces sensor life, which is unfavorable for practical applications [2,7]. Therefore, it is essential to develop high-performance NO$_2$ sensors operating at room temperature (RT) [8].

Porous silicon (PS) has been considered as a very promising semiconductor material over the past years due to its widespread applications such as solar cells, photonic crystals, photovoltaic devices, and biomedical sensors [9–11]. Moreover, through an extensive research in gas sensitive materials, the PS has attracted increasing attention as a favorable candidate because of its huge specific surface area and high surface chemical reactivity at RT [12]. In this respect, previous reports have demonstrated that the PS-based gas sensors can respond to various gases at RT, like NO$_2$ [13], NH$_3$ [14], SO$_2$ [15], H$_2$S [16], acetone [17], ethanol [18], methanol [19], and isopropanol [20]. The morphology, pore diameter, geometric shape, porosity and porous layer thickness are known to be the main factors determining the PS gas-sensing properties [21,22].

In recent years, gas-sensing characteristics of Meso-PS (pore size 10–50 nm) and "classical" Macro-PS (pore size > 200 nm) have been extensively studied [23–25]. It is found that the NO$_2$-sensing behavior is highly dependent on PS microstructure features. For instance, the Meso-PS with branching and interconnecting pore channels presented a very slow recovery rate even irreversible response, which was closely related to the problem of gas molecules out of the pores. Conversely, "classical" Macro-PS can remarkably reduce the recovery time. However, the porosity was sharply decreased that meaning the reduction of adsorption sites, ultimately resulting in a low response sensitivity when used as a gas sensor.

For achieving a good sensitivity with a rapid response–recovery rate, it is reasonable to infer the superior PS microstructure should exhibit huge specific surface area together with high accessibility of gas molecules to the material surface by diffusion [26]. It is worth

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mentioning that the PS with intermediate size pores (50–200 nm) are large enough to allow easy diffusion of gas molecules, but small enough to preserve the large specific surface area for obtaining a strong response [27]. Hence, the Intermediate-PS is considered as a very attractive compromise, which could combine the respective advantages of Meso-PS and "classical" Macro-PS [28]. Therefore, Intermediate-PS is very promising for gas-sensing application, which has not been extensively and systematically studied. In our previous work, a kind of Intermediate-PS based on the n-type silicon substrate has been successfully prepared and exhibited preeminent NO_2-sensing properties (e.g. good sensitivity and fast response–recovery speed) at RT [29]. So, we believed that the Intermediate-PS based on the p-type silicon substrate can also exhibit superior sensing performances versus NO_2.

PS is mainly produced by the electrochemical etching of the crystalline silicon wafer in the HF-based solution because this method has the simple and economic benefits compared to e-beam lithography [30,31]. The anodization conditions (doping concentration of the silicon wafer, HF concentration, etching current density, anodization time, and the presence of surfactant and oxidant) always play critical roles in the PS microstructure features (morphology, geometry, porosity, and porous layer thickness) [32–34]. Besides, the Intermediate-PS is generally considered difficult to form on the silicon substrate due to its preparation condition is usually limited to a very narrow transition region between electropolishing and porous layer formation [22,35]. Some groups have reported several preparation methods could produce p-type PS with the pore diameter belongs to the intermediate size regime [36–38]. However, these p-type Intermediate-PS microstructures did not display uniformly ordered pore channels. In our point of view, the p-type Intermediate-PS combines large porosity with well-separated pore arrays could be ultimately obtained via matching proper anodization conditions.

In this work, a kind of p-type Intermediate-PS was successfully prepared via a simplified and cost-effective galvanostatic electrochemical etching method. The procedure was highly reproducible, and did not require additional steps like post-etching chemical treatments. Subsequently, the fabricated PS gas sensor was evaluated by detecting NO_2 at the sub-ppm level. The Intermediate-PS showed superior NO_2-sensing performances at RT, including strong response, very rapid response–recovery characteristics and perfect repeatability, which can be attributed to its favorable microstructure features. To the best of our knowledge, the p-type Intermediate-PS has seldom been investigated for NO_2 detection. The plausible sensing mechanism was also introduced in detail.

2. Experiment

2.1. Synthesis and characterization

In our experiments, p+-type silicon wafers (boron-doped, single polished, resistivity 3 mΩ cm, (1 0 0) orientation, thickness 400 μm) were diced into small pieces in shape with 24 mm × 8 mm. Before anodization, the wafers were ultrasonically washed with acetone, ethanol and deionized water successively for 20 min to remove the organic contaminants. Then, the wafers were immersed in 5 wt% aqueous HF for 15 min to remove the native oxide. After cleanup, PS layer was formed on the silicon substrate via a galvanostatic electrochemical etching method. Each wafer was held vertically in the position by clamping in a home-made Teflon double-tank cell, determining the exposed surface area of 64 mm². The schematic diagram of the electrochemical anodization cell is shown in Fig. 1. Herein, a pair of platinum (Pt) electrodes were dipped in the electrolyte and placed parallel to the wafer arranging to the anode and cathode, respectively. The electrolyte was
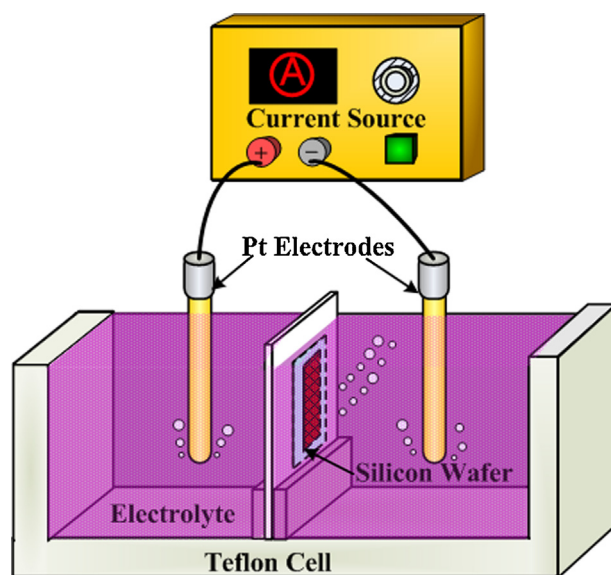

Fig. 1. Schematic diagram of electrochemical etching cell for preparing Intermediate-PS.

based on a mixture of 7 wt% aqueous HF (40 wt% HF was diluted with deionized water), 4 mM $KMnO_4$ oxidant, and 2 mM sodium dodecyl sulfate (SDS) surfactant. The etching current density was 60 mA/cm² supplied by a constant current source (ATTEN, PCR70). The anodization process was performed for 15 min in the dark and at RT. Then, each PS sample was thoroughly cleaned with deionized water to purge any residue in the pores and dried naturally in the ambient atmosphere.

Porosity is defined as the fraction of voids within the porous structure, determining the specific surface area of PS [39]. The average porosity (p) and layer thickness (d) of the prepared PS can be effectively estimated by the gravimetric method (Eqs. (1) and (2)) [40].

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

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

where m_1 is the mass of the silicon wafer before anodization, m_2 is the mass just after anodization, and m_3 is the mass after dissolution in a 1 wt% solution of KOH. Besides, ρ and S are the bulk density of the silicon wafer and the PS surface area, respectively. Experimentally, each sample was weighted at least three times via an electronic balance (LIBROR, AEG-120, with the least count of 10^{-4} g).

The morphology and structure of prepared PS samples were observed by using field emission scanning electron microscope (FESEM, Hitachi S-4800 with an accelerating voltage of 5.0 kV, respectively). Plan view micrograph shows the (1 0 0) plane, and the cross-section view micrograph shows the pores in the (1 1 0) cleavage plane. Furthermore, Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 670 spectrometer) is a powerful tool for determining the bonding configuration types of the PS surface. The spectrum was recorded ranging from 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1}.

2.2. Sensor preparation and measurement

For the fabrication of gas sensors, Pt thin films were deposited on the PS surfaces as contact electrodes by using RF magnetron sputtering system (DPS-III). The length, width, thickness, and gap