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Characterization of silicon nanoporous pillar array as room-temperature capacitive ethanol gas sensor

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Abstract

A room-temperature capacitive ethanol sensor was fabricated based on a silicon nanoporous pillar array (Si-NPA) and the corresponding ethanol gas sensing properties were studied. With ethanol concentration changing from 0 to 500 ppm, a capacitance increase over 430% was achieved at a signal frequency of 200 Hz. The device response was found to be concentration dependent, lower at low concentration and higher at high concentration. The response and recovery times measured at 50 ppm ethanol concentration were about 15 and 30 s, respectively. The sensor showed long-term stability; the capacitance measured under the same conditions remained almost unchanged during 40-week storage. The high performances of Si-NPA ethanol gas sensors were attributed to the enlarged sensing area arising from the numerous nanopores, the effective mass transportation pathway brought by the regular pillar array, and the stable surface status resulted from the strong iron-passivation. Our results indicated that Si-NPA might be a promising sensing material to fabricate practical room-temperature ethanol gas sensors.

Keywords: Silicon nanoporous pillar array (Si-NPA); Ethanol gas sensor; Capacitive

1. Introduction

Owing to its large specific surface area and technological compatibility with modern typical silicon arts, porous silicon (PS) as a promising gas or humidity sensing material has attracted much attention in the past several years [1–7]. Although the detailed geometrical features, which might play key roles in deciding sensor performances, were highly dependent upon the preparing conditions, the integral sponge structure was the most important and commonest characteristics of all PS samples [1,2]. Just as found in detecting humidity [6,7], nitrogen dioxide [8–11], ethanol gas [12–14], and various organic vapors [3,15,16], PS-based sensors showed an improved sensitivity but a relatively long response time, which were attributed to the greatly enlarged sensing area formed in PS and the absence of effective gas transportation pathways in the sponge structure, respectively. In previously published papers, we have reported that an effective pathway for gas transportation could be built in a silicon nanoporous pillar array (Si-NPA) [17,18], which was a triple hierarchical structure constructed on single crystal silicon wafers, and excellent humidity sensing properties including high sensitivity and fast response rate were achieved in the Si-NPA-based sensors [19,20]. In this paper, the room-temperature capacitive ethanol gas sensing properties of Si-NPA were studied and the underlying mechanisms were analyzed based on its unique surface structure, morphology, and physical properties. Our experiments strongly indicated that Si-NPA might be a promising ethanol gas sensing material for practical applications.

2. Device fabrication and experimental

Si-NPA used here was prepared by hydrothermally etching the (1 1 1) oriented, boron doped ($\rho = 0.015\ \Omega$ cm) single crystal silicon wafers in the solution of hydrofluoric acid containing ferric nitrate [17,18]. The microstructure and surface morphology of Si-NPA were investigated by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The device design was demonstrated as the schematic diagram presented in Fig. 1. The devices were fabricated on 20 mm × 20 mm Si-NPA squares. The electrodes constructing a parallel plate capacitor were manufactured by

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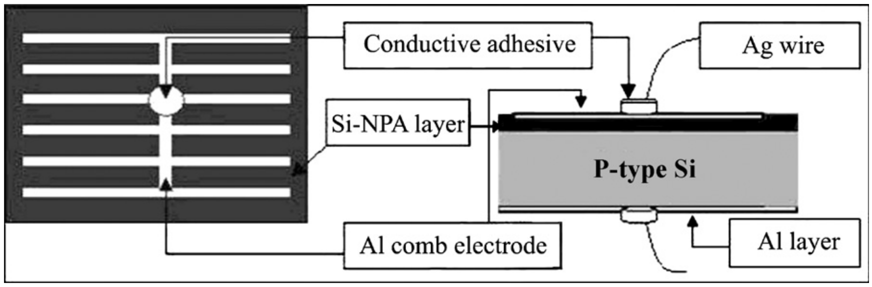

Fig. 1. A schematic diagram of a capacitive Si-NPA ethanol sensor.

magnetron sputtering a uniform aluminum layer on one side, and an aluminum comb electrode on the other side of the square. Silver wires were chosen as the leads to connect the electrodes and the testing instrument through conductive adhesive. The ethanol-sensing measurements were carried out by placing the device in a chamber which was connected to a container of vapor mixtures by a tube. An inductance–capacitance–resistance (LCR) multi-frequency meter was used to probe the variation of the capacitance of Si-NPA with ethanol concentration. All these electrical measurements were carried out under atmospheric pressure and at room temperature.

3. Results and discussion

Fig. 2(a) demonstrates the typical surface morphology of Si-NPA obtained by FE-SEM, where a regular array composed of large quantities of well-separated, quasi-identical silicon pillars is clearly observed. This morphological feature was significantly different from the integral sponge structure of traditional PS. The pillar height and the distance between two neighboring pillars were evaluated to be ∼2.5 and ∼4.0 μm, respectively. Obviously, the valleys around every pillar are intercommunicated and formed an effective pathway for vapor transportation into or out of Si-NPA. Further investigation on the microstructure of Si-NPA by TEM was presented in Fig. 2(b). Clearly, all the silicon pillars observed in Fig. 2(a) are nanoporous, exhibiting a disorderly distributed nanoporous structure similar to that observed in traditional PS. This predicted the similarity of the surface physical and chemical properties between Si-NPA and traditional PS. Together with the fact that the pore walls were composed of silicon nanocrystallites, the integral picture of the structure of Si-NPA could be described as a hierarchical structure composed of the array of silicon pillars, the sponge structure of nanopores, and the silicon nanocrystallites composing the pore walls [18]. Deduced from the above structural characteristics, Si-NPA could be highly expected as an ethanol-sensing material with promising performances.

The capacitive ethanol-sensing properties of Si-NPA were measured at room temperature by placing the device in a testing chamber. The inner ethanol concentration of the chamber was controlled to change from null to 500 ppm with a step of 50 ppm. It has been found that there exists a dependency of the capacitance on the applied signal frequency, which agrees with the results of similar researches reported by others [13]. In the present experiment, when the frequency for detection was chosen to be 20, 100, 200, 1000 and 10,000 Hz, the corresponding ratios of the capacitances obtained at 500 and 0 ppm were 2.35, 2.14, 5.30, 1.63 and 1.28, respectively. Clearly the device response to ethanol gas was more sensitive at a frequency of 200 Hz and therefore this frequency was chosen as the applied signal frequency in the following experiments. The experimental capacitance versus ethanol concentration characteristic is depicted in Fig. 3. With increasing the ethanol concentration from null to 500 ppm, the capacitance changed from ∼42.31

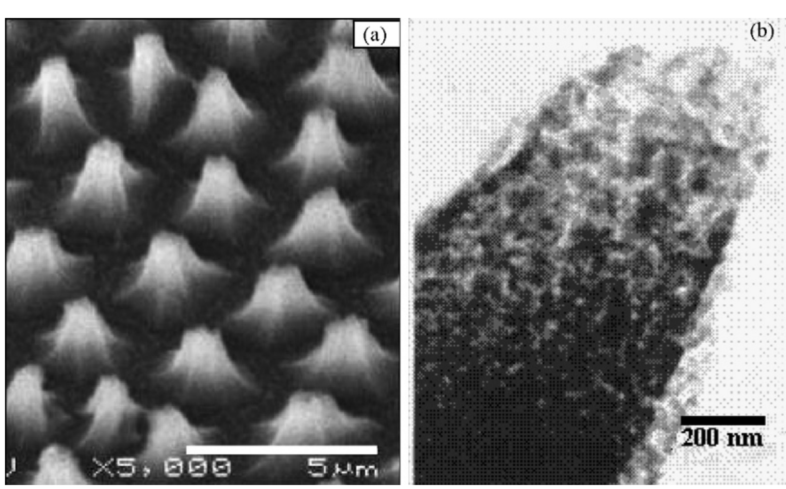

Fig. 2. (a) Typical surface morphology of Si-NPA obtained by FE-SEM with the sample being titled at an angle of 30° and (b) a TEM image of the upper part of an individual porous pillar.