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介孔硅与大孔硅的结构、电学和气敏特性

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摘要: 采用双槽电化学腐蚀法在P型单晶硅表面制备两种多孔硅. 根据它们的孔径将它们分为介孔硅和大孔硅. 使用扫描电子显微镜(SEM)观察两种多孔硅表面和断面形貌, 介孔硅和大孔硅的表面化学键用傅里叶变换红外(FTIR)光谱仪来研究, 通过*I-V*特性测试表征两种多孔硅电学特性, 随后在室温下测试其气敏特性. 结果表明: 介孔硅具有较高的气体灵敏度, 大孔硅具有较好的气体响应恢复特性. 介孔硅对NO₂气体具有较好的选择性, 大孔硅对NH₃气体具有较好的选择性.

关键词: 介孔硅; 大孔硅; 室温; 气敏特性

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Microstructure, Electrical and Gas Sensing Properties of Meso-Porous Silicon and Macro-Porous Silicon

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Abstract: Two different kinds of porous silicon (PS) were grown by electrochemical corrosion in a double-tank cell on the surface of single-crystalline P-type silicon. According to their pore sizes, they were denoted as meso-porous silicon (meso-PS) and macro-porous silicon (macro-PS). The surface and cross-section morphologies of the PS were observed by scanning electron microscope (SEM). The surface chemical bonds of the meso-PS and macro-PS were investigated by Fourier transform infrared (FTIR) spectroscopy. The electrical properties of the PS were studied by measuring the *I-V* characteristics. The gas sensing properties of meso-PS and macro-PS were thoroughly measured at room temperature. Meso-PS has much higher sensitivity, while macro-PS has better response-recovery characteristics. Meso-PS shows better selectivity for NO₂, while macro-PS shows better selectivity for NH₃.

Key Words: Meso-porous silicon; Macro-porous silicon; Room temperature; Gas sensing property

1 Introduction

Several materials with large specific surface areas, such as polymer membranes,¹ carbon nanotubes,^{2,3} and metal oxide⁴⁻⁶ have been studied as prospective candidates for future gas sensors. Porous silicon (PS) is an especially interesting material with large specific surface area,⁷ which is easily produced by electrochemical process.^{8,9} PS formed by this method have diameters varying from tens nanometers¹⁰⁻¹² to a few of microme-

ters.^{13,14} It has been classified according to the pore size as micro-PS (≤ 2 nm), meso-PS (2–50 nm), and macro-PS (> 50 nm).¹⁵ As the specific area of PS may be as high as 700–800 m²·cm⁻³,¹⁶ it can be used as gas sensor. Recently, many chemical sensors using PS have been reported to be operated at room temperature,¹⁷⁻¹⁹ which is not possible for other semiconductor gas sensors. Additionally, it is easy to fabricate with an advantage of controlling the surface morphology through the varia-

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tion of the formation parameters. Most importantly, PS is compatible with silicon integration technology.²⁰

However, PS contains a large number of interface states and volume traps. This leads to the instability of electro-physical parameters of gas sensor based on porous silicon with poor gas sensing properties due to the significant Fermi-level pinning.²¹ To overcome the defects of PS, a few studies on the modified layer and the catalyst deposition on porous silicon surface were reported.^{22–24} Unfortunately, reversibility and response-recovery time are still the two issues which restrict the PS for practical applications. Actually, the changing of the microstructure of the PS may bring large variation in the gas sensing properties. However, there are only a few articles reporting on the relationship between the microstructure and the gas sensing properties.^{25,26}

In this work, meso-PS and macro-PS were made. We investigated the gas sensing properties of PS at room temperature and focused on both response-recover characteristics and the effect of the microstructure on sensitivity.

2 Experimental

Meso-PS and macro-PS were formed by electrochemical corrosion²⁷ of a (100)-oriented mono-crystalline P⁺-type silicon wafer with 1×10^{-2} – 2×10^{-2} $\Omega \cdot \text{cm}$ resistivity and a (100)-oriented mono-crystalline P-type silicon wafer with 10–15 $\Omega \cdot \text{cm}$ resistivity in a double-tank cell, respectively. The mass fractions of HF, C₂H₅OH, and dimethylformamide (DMF) were 40%, 99.7%, and 99.5%, respectively. The preparing conditions of the PS are shown in Table 1.

Pt electrodes of dimensions 3 mm×3 mm were deposited on the top of PS gas sensor using dc magnetron sputtering method. The base pressure was 5×10^{-4} Pa and the sputtering pressure was 2 Pa. The sputtering gas was Ar. The sputtering power was 90 W. The sputtering time was 10 min. Fig.1 is the schematic diagram of the PS gas sensor.

The average porosity (ε), i.e., the void fraction in the porous layer, can be obtained by gravimetry via Eq.(1):

$$\varepsilon = \frac{m_1 - m_2}{m_1 - m_3} \quad (1)$$

Table 1 Preparing conditions of the meso-PS and macro-PS

Sample	Electrolyte (volume ratio)	Current density (mA·cm ⁻²)	Etching time min
meso-PS	HF:C ₂ H ₅ OH (1:1)	80	30
macro-PS	HF:DMF (1:2)	100	5

Fig.1 Schematic diagram of the PS gas sensor

where m_1 is the mass of the sample before the etching, m_2 is the mass of the sample after the formation of the PS layer, and m_3 is the mass of the sample after the removal of the PS layer in KOH solution (1% , mass fraction). The electronic balance (AR1400, OHAUS, USA) has an accuracy of 0.0001 g. The morphology of PS layers was measured by a field emission scanning electron microscope (FESEM, Nanosem 430, FEI, USA). The surface chemical bonds of the PS were studied by Fourier transform infrared spectroscopy (FTIR, NEXUS470, Thermo, USA). Current–voltage (I – V) characteristics of the PS samples were tested by potentiostat (ZF-9, Zheng Fang Electronics Corporation, China). Gas sensing characteristics of PS samples was measured at room temperature. In this process, they were placed in a chamber of 30 L. Test gas was precisely inserted by using an injector. The gas detection sensitivity (S) of the sensor device has been evaluated using the relation:

$$S = R_r/R_a \text{ or } S = R_o/R_a \quad (2)$$

where R_r , R_o , and R_a are resistances of the sensor device in reducing gas, oxidizing gas, and the ambient atmosphere, respectively.

The gas baseline shift (T) of the sensor device has been evaluated using the relation:

$$T = R_{re}/R_{in} \quad (3)$$

where R_{in} and R_{re} are resistances of the sensor device before gas injected and after gas removed, respectively.

3 Results and discussion

3.1 Morphology of meso-PS and macro-PS samples

Fig.2(a, b) show the SEM photographs of two different kinds of PS layers with a symmetrical hole-shaped frame. It can be seen that the average pore sizes are 20 nm and 1.5 μm , respectively, so the two different kinds of PS samples respectively belong to meso-PS and macro-PS. Fig.2(c, d) present the SEM images of the cross-section of PS. The meso-PS shows a tree branch porous silicon structure, while the macro-PS shows an orderly uniform porous silicon structure. The porosity is about 76.8% and 39.3% for meso-PS layer and macro-PS, respectively. As there is lots of silica which has not been etched, the macro-PS has lower porosity.

3.2 FTIR analysis of meso-PS and macro-PS samples

FTIR spectra of the meso-PS and macro-PS in a range of 850–2200 cm^{-1} are shown in Fig.3. Both the spectra of the meso-PS and macro-PS demonstrate the peaks of Si–O–Si stretching mode (1020–1260 cm^{-1}) and the weak peaks of Si–H₂ oscillation mode (deformation mode around 850–900 cm^{-1} and stretching mode around 2100 cm^{-1}), which agree well with literature.²⁸ It is noted that the density of the surface chemical bonds of meso-PS is larger than that of the macro-PS extending on the entire spectral range. The reason for the phenomenon is that the specific surface area of the meso-PS is larger than that of the macro-PS. As the meso-PS has more surface

Fig.2 SEM images of the meso-PS (a, c) and macro-PS (b, d)
(a, b) surface morphologies; (c, d) cross-section morphologies

chemical bonds, more gas can be absorbed on its surface and its sensitivity may be higher than that of the macro-PS.

3.3 I - V characteristics of meso-PS and macro-PS samples

Fig.4 shows I - V characteristics of the meso-PS and macro-PS. The voltage was applied between the two Pt electrodes. As the work function of Pt is larger than that of the PS, there is a high-conductance region on the surface of PS. The electrical behavior of the I - V curves exhibits an ohmic contact. The I - V characteristic curves are linear. It also can be seen from Fig.4 that the resistance of the meso-PS is higher than that of the macro-PS. On one hand, by increasing the porosity, the surface

area increases. The higher surface area causes higher internal length for flowing charge carriers and the surface resistivity becomes higher. On the other hand, as the porosity increases, the effect of the carriers captured by the pore wall is enhanced. So the resistance of the meso-PS is higher than that of the macro-PS.

3.4 Gas sensing properties of meso-PS and macro-PS samples

The gas sensing properties of the meso-PS and macro-PS towards 5×10^{-5} (volume fraction) NH_3 were tested at room temperature. As shown in Fig.5 the resistance values of PS gas sensors increase to stable values at first when adsorbing NH_3 . After disengagement from the gas environment, the resistance values decrease gradually to stable values. As NH_3 is a reducing gas, it makes local and partial reduction of PS surfaces which

Fig.3 FTIR spectra of the meso-PS (a) and macro-PS (b) in a range of $850\text{--}2200\text{ cm}^{-1}$

Fig.4 I - V characteristic curves of the meso-PS (a) and macro-PS (b)

Fig.5 Sensitivity (S) curves of the meso-PS (a) and macro-PS (b) to 5×10^{-5} (volume fraction) NH_3 at room temperature

$$S = R_s/R_a$$

causes the decrease of defect density. These defects play the role in electron traps into which electrons relax.^{29,30} The decrease of the number of electron traps will induce a large number of free electrons on the surfaces of PS and the number of holes reduces greatly, so that resistance values increase. Therefore, it seems that the electron traps which are diminished by partial reduction of PS in the presence of NH_3 are responsible for the decrease of free charge carriers in P-type PS.

The gas sensing properties to NH_3 are shown in Table 2. As shown in Table 2, the sensitivity of meso-PS to NH_3 is much higher than that of macro-PS. It is also clear from Table 2 that the macro-PS shows faster response-recovery than the meso-PS at room temperature. The porosity of meso-PS is 76.8%, while for macro-PS it is 39.3%. The relative higher porosity can result in higher specific surface area. Thus the meso-PS can absorb more gas, and show higher sensitivity. From the SEM images shown in Fig.2(c, d), it is obvious that the pores of macro-PS are more orderly and uniform than those of meso-PS. It may be the reason for the better response-recovery characteristics of macro-PS.³¹

As the poor reversibility of the PS, the resistance can not often recover to the initial value.³² So there are only a few articles^{32–34} which reported good dynamic response of PS. But in our research, macro-PS shows a good dynamic response characteristic. Fig.6 shows the dynamic responses of macro-PS to NH_3 gas in various concentrations. As shown in this figure, the measured resistance increases upon exposure to NH_3 gas. Notably, the resistance could almost recover to its initial value after removal of NH_3 , indicating a good reversibility of this material. The sensitivity values of the macro-PS upon exposure to 25×10^{-6} , 50×10^{-6} , 100×10^{-6} , and 200×10^{-6} (volume fraction) NH_3 are 2.90, 4.20, 10.24, and 11.65, respectively.

Selectivity is an important factor in gas sensing, and the sensor has to present rather high selectivity for its application. It is

Table 2 Gas sensing properties of meso-PS and macro-PS to NH_3

Sample	$S/(\text{a.u.})$	$T/(\text{a.u.})$	Response time/s	Recovery time/s
meso-PS	15.12	6.26	1717	1190
macro-PS	4.20	1.00	85	477

Fig.6 Dynamic responses of macro-PS to various NH_3 concentrations at room temperature

Fig.7 Sensitivity of meso-PS (a) and macro-PS (b) to various gases (5×10^{-5}) at room temperature

known to all that a PS sensor responds to other gases as well. For this reason, we investigated the sensitivity of the meso-PS and macro-PS sensors to other gases at room temperature. The gas sensitivity of meso-PS and macro-PS to various gases at room temperature are compared and the results are shown in Fig.7. It can be seen that the sensitivity of the meso-PS to NO_2 is much higher than that to other gases, while the sensitivity of the macro-PS to NH_3 is much higher than that to other gases. Furthermore, the sensitivity of meso-PS to all of these gases is higher than that of macro-PS, especially to NO_2 . The different selectivity characteristics of different PS may relate to the dangling bonds on the PS surface. As it is shown in the Fig.3, the peaks of $\text{Si}-\text{H}_x$ and $\text{Si}-\text{O}-\text{Si}$ bonds on the surface of meso-PS are stronger than those of the macro-PS. The $\text{Si}-\text{H}_x$ bonds and $\text{Si}-\text{O}-\text{Si}$ bonds play a major role in the adsorption of NO_2 and NH_3 ,^{35,36} respectively. Therefore, the sensitivity of the meso-PS to testing gases is higher than that of the macro-PS. It is also shown that the density of $\text{Si}-\text{H}_x$ bonds on the macro-PS surface is very small. That may explain the selectivity of the macro-PS to NH_3 .

4 Conclusions

Meso-PS and macro-PS layers were fabricated respectively on single crystal P^+ -type silicon and P-type silicon surfaces by electrochemical corrosion in a double-tank cell. Then Pt electrodes were deposited on PS layers by dc facing target magnetron sputtering. The normal pore sizes of the meso-PS and macro-PS are about 20 nm and 1.5 μm , respectively. The macro-PS shows an orderly uniform porous silicon structure. The $I-V$ characteristic curves are linear. The meso-PS shows higher sensitivity, and the macro-PS shows better response-recovery characteristics. The two different kinds of PS exhibit different selectivity.

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