The light-enhanced NO_2 sensing properties of porous silicon gas sensors at room temperature*

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The NO_2 gas sensing behavior of porous silicon (PS) is studied at room temperature with and without ultraviolet (UV) light radiation. The PS layer is fabricated by electrochemical etching in an HF-based solution on a p^+-type silicon substrate. Then, Pt electrodes are deposited on the surface of the PS to obtain the PS gas sensor. The NO_2 sensing properties of the PS with different porosities are investigated under UV light radiation at room temperature. The measurement results show that the PS gas sensor has a much higher response sensitivity and faster response–recovery characteristics than NO_2 under the illumination. The sensitivity of the PS sample with the largest porosity to 1 ppm NO_2 is 9.9 with UV light radiation, while it is 2.4 without UV light radiation. We find that the ability to absorb UV light is enhanced with the increase in porosity. The PS sample with the highest porosity has a larger change than the other samples. Therefore, the effect of UV radiation on the NO_2 sensing properties of PS is closely related to the porosity.

Keywords: gas sensor, ultraviolet radiation, porous silicon, porosity

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1. Introduction

With the continuing development of industry, air pollution has become more and more serious. The detection of toxic gases is very important both for the environment and human health.[1−3] Porous silicon (PS) has drawn considerable attention for gas sensing applications at room temperature because of its amazingly large surface area, luminescence properties, and compatibility with silicon-based technologies.[4] It has been reported that many kinds of gases (such as NH_3, NO_2, and H_2) can be detected by PS,[5] and in the meantime it can be used as the substrate material to realize nanosensors with relatively high sensitivity at room temperature.[6] Such properties mean that PS is utilized as a promising gas sensor, however, it still has certain limitations in gas sensing applications, such as low sensitivity and a long recovery time.[7,8]

Recently, many investigators have reported that the working temperatures of some films used as gas sensor materials, like SnO_2,[9−11] ZnO,[12−14] Cr_2O_3,[15] and WO_3,[16] can be reduced to room temperature under ultraviolet (UV) light illumination. Comini *et al.*[8] showed that exposure to UV radiation results in a decrease in the response and recovery times of tin oxide gas sensors at low temperature, with no poisoning effect when NO_2 comes into contact. Anothainart *et al.*[9] concluded that illumination at room temperature enhances the desorption of the previously adsorbed NO_2 species at the SnO_2 surface. Liang *et al.*[17] demonstrated that the gas sensitivity of UV light-assisted gas sensors is controlled primarily by the surface-to-volume ratio and the photo-generated charge efficiency. The effects of photoexcitation are concentrated on the increase in the density of the free carriers throughout the material, the decrease in the intergrain barrier height, and the increase in the probability of tunneling through the intergrain barriers by reducing the depletion layer widths in the adjacent grains.[9]

In the present work, PS films of different porosities are prepared. We mainly investigate the NO_2 sensing properties of PS films with and without UV illumination. The relation between porosity and light irradiation, and the mechanism with irradiation, is also discussed.

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2. Experimental details

First, porous silicon layers were formed by conventional electrochemical dissolution in a double-tank cell on the surfaces of single-crystalline p^+-type silicon substrates (380 nm thickness, 0.01–0.012 Ω·cm resistivity) for 30 min. The anodizing solution was obtained by mixing 50 vol.% aqueous HF with ethanol. The etching current densities were 40 mA/cm^2, 60 mA/cm^2, and 80 mA/cm,^{2} respectively. Accordingly, we denoted the three kinds of samples as PS-40, PS-60, and PS-80, respectively. Then, the electrical contacts (Pt films) of the sensing element were deposited on the porous silicon layers by using direct-current (DC) magnetron sputtering (DPS-III) to obtain the PS gas sensors. A schematic diagram of the gas sensor is shown in Fig. 1(a).

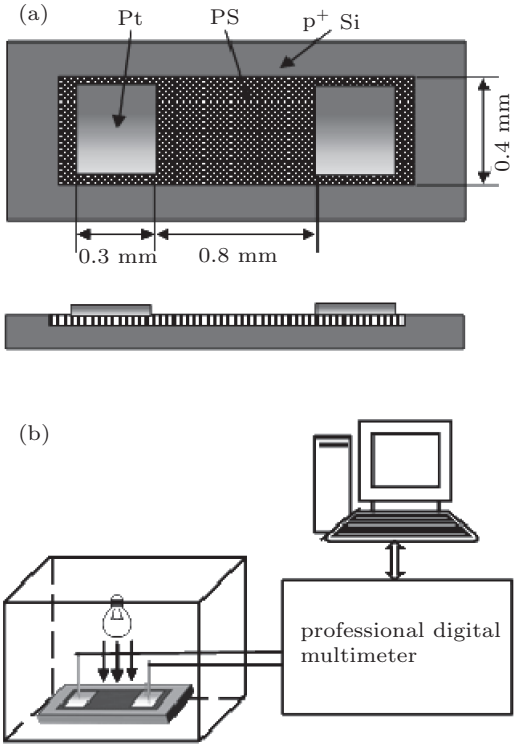


Fig. 1. Schematic diagrams of (a) the PS gas sensor and (b) the gas sensing test system.

The porosities of the PS samples were measured by using the gravimetric method,[18] and the morphologies of the PS layers were measured by a field emission scanning electron microscope (FESEM, FEI Nanosem 430). To measure the sensitivity to NO_2 under UV illumination, we placed the samples in a computer-controlled static gas sensing characterization system, which included a test chamber, a UV lamp, a professional digital multimeter, and a data acquisition system. A schematic diagram of the gas sensing test system is shown in Fig. 1(b). The sensors were placed on a plate fixed in the test chamber. NO_2 was injected into the test chamber using a syringe to obtain the desired concentration, and the sensor was recovered by opening the side cover of the test chamber. We used a UNIT UT70D professional digital multimeter to monitor the resistances of the sensors in the whole measurement process. The resistance data were recorded on a personal computer. Based on the above sensing measurements, the photoelectric sensing measurement was carried out using 365 nm UV light irradiation, which was provided by a 9 W UV lamp. Then, we measured the gas sensing characteristics with and without UV irradiation at different NO_2 concentrations. The sensor response intensity (S) is defined as $S = R_0/R$, where R and R_0 are the resistances of the sensor in the NO_2 gas and in the clean air, respectively. The response time is defined as the time when 90% of the total resistance is reached. Conversely, the recovery time is the time when 90% of the resistance is recovered.

3. Results and discussion

Figure 2 shows SEM images of the surfaces of the PS layers. The distribution of the pores is uniform. We measure the porosities of the PS samples using the gravimetric method. The porosities are 65.2%, 71.1%, and 76.8% for PS-40, PS-60, and PS-80, respectively. As the etching current density grows, the porosity of the PS increases.

The photoelectric characteristics of the samples are investigated before the gas sensing measurement. The UV photoresponses of these samples in air are shown in Fig. 3. The initial resistances are about 8 MΩ, 15 MΩ, and 24 MΩ for PS-40, PS-60, and PS-80, respectively. The resistance of PS-80 is the highest because its porosity is the highest among the samples and it has the largest surface-to-volume ratio. When the samples are irradiated with UV light, their resistances all decrease sharply because their carrier concentrations increase quickly, which is induced by the photo-generated electrons and holes. From Fig. 3, we can see that the resistance change of PS-80 is the largest, followed by PS-60, while S-40 has the smallest change. The reason for this may be that the high porosity can help PS-80 absorb photon more efficiently, and thus more electrons and holes are created.

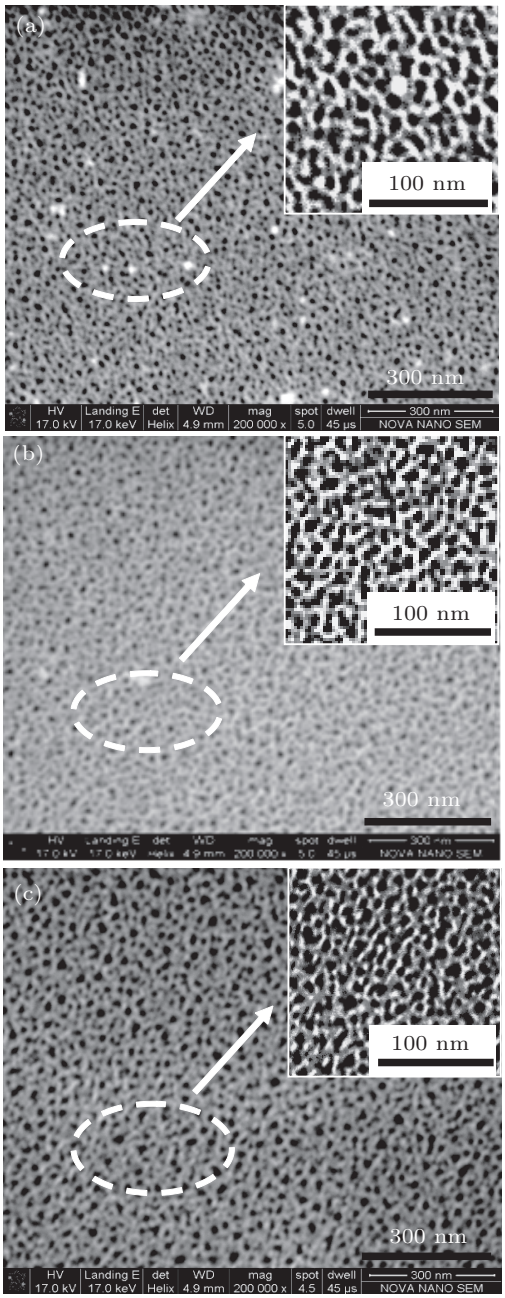


Fig. 2. SEM images of the PS layers of (a) PS-40, (b) PS-60, and (c) PS-80.

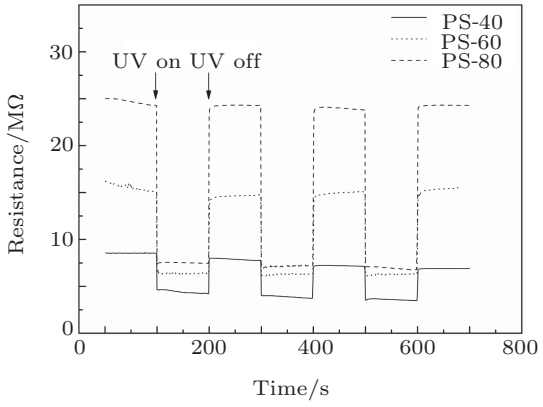


Fig. 3. Resistance characteristics of PS-40, PS-60, and PS-80 in air under 365 nm UV irradiation.

After the UV light is turned off, the resistance increases quickly. This is due to the electron–hole recombination in the particle. In conclusion, under the same irradiation intensity, the photo-generated charge quantity increases in the order of PS-40 < PS-60 < PS-80, which is consistent with the increase in porosity.

The NO_2 sensing properties of the PS gas sensor are measured with and without UV light irradiation. The typical response–recovery curves of the PS gas sensor to NO_2 at different concentrations with and without irradiation are shown in Fig. 4. From this figure, it can be seen that the sensing film shows good sensitivity when it is exposed to NO_2 at room temperature, especially under UV irradiation. The response of most gas sensors is due to the changes in carrier concentration, which are usually induced by analyte adsorption on the surfaces of the sensing materials. The PS fabricated in the experiment behaves as a p-type semiconductor. When it contacts NO_2, NO_2 acts as a kind of oxidizing gas, which will capture the electrons from the sensing material. Thus the concentration of holes will increase, reducing the depletion layer widths in the adjacent grains and increasing the conducting channel widths. The conductivity of the PS increases accordingly.[7] With the 365 nm ultraviolet illumination, because of the fast electron–hole generation process, the carrier concentration in the nanocrystal increases rapidly. This will facilitate the interaction of the surface of the semiconductor with the gas and speed up the reactions.[18] NO_2 can capture more electrons, which is attributed to the further increase in conducting channel width. The conductivity of the PS then increases further, and as a result, UV irradiation can improve NO_2 gas sensing performance at room temperature.

Figure 5 shows the response and recovery characteristics of PS gas sensors to 1 ppm NO_2 with and without UV irradiation. We can see that the response and recovery times are both improved. It has been demonstrated that the charge exchange between the sensor element and analyte is a photocatalytic oxidizing process.[17] The photogenerated carriers can facilitate reduction and oxidation chemistry on the material surface.[19] Under UV irradiation, a large number of photo-generated electrons and holes exist in the PS. It is therefore easy to conclude that the photogenerated carriers on the PS surface greatly contribute to the improvement in response and recovery performance.

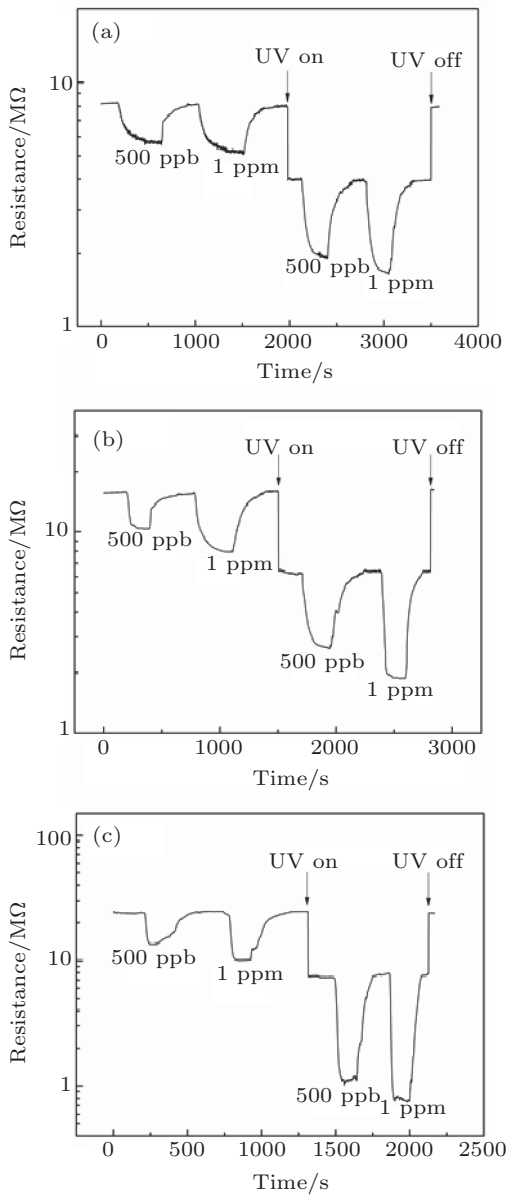


Fig. 4. Dynamic responses of (a) PS-40, (b) PS-60, and (c) PS-80 to various concentrations of NO_2 with and without 365 nm UV irradiation.

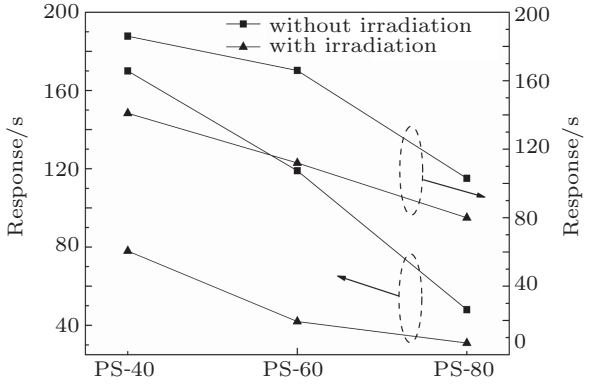


Fig. 5. The response and recovery times of PS gas sensors to 1 ppm NO_2 with and without UV irradiation.

Figure 6 shows the sensitivities of the PS gas sensors to 500 ppb and 1 ppm NO_2 with and without the irradiation. The sensitivities of PS-40, PS-60, and PS-80 to 1 ppm NO_2 with (without) irradiation are 2.5 (1.6), 3.4 (1.9), and 9.9 (2.4), respectively. This demonstrates that the gas response of the PS sensor to NO_2 with the irradiation is larger than that without the irradiation. Under the 365 nm UV illumination, the carrier concentration increases quickly, which is induced by the photo-generated electrons and holes. This facilitates the interaction of the surface of the semiconductor with the gas. As NO_2 absorbs more electrons, the depletion layer widths decrease further in the adjacent grains, and the conducting channel widths increase further, thus the conduction of the PS increases further. The light irradiation can improve the sensitivity further with the increase in porosity. The larger porosity means that PS-80 has a higher surface-to-volume ratio, which is related to the photo-generated charge efficiency. The sensing process of the gas sensor should include two parts: the adsorption of the analyte on the sensor element (receptor function) and the charge exchange between the analyte and the sensor element (transducer function).[20] The PS with a higher surface-to-volume ratio would adsorb more analyte, leading to a higher gas sensitivity. The PS-80 has the highest photo-generated charge efficiency. Therefore, the sensitivity of PS-80 changes much more than that of the other samples under UV light irradiation.

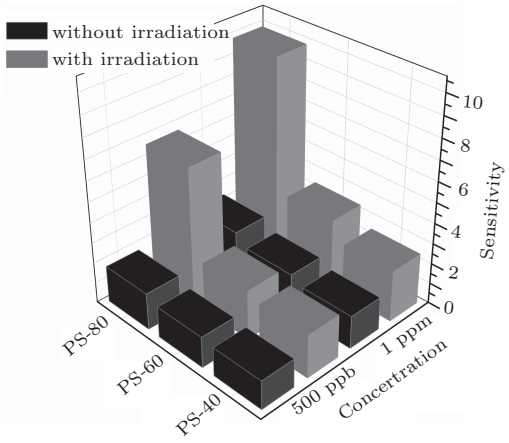


Fig. 6. The sensitivities of PS gas sensors to 500 ppb and 1 ppm NO_2 with and without UV irradiation.

4. Conclusion

Three groups of PS samples were obtained by electrochemical dissolution in a double-tank cell on

the surfaces of single-crystalline p^+-type silicon substrates with etching current densities of 40 mA/cm^2, 60 mA/cm^2, and 80 mA/cm^2 for 30 min, respectively. Under the same irradiation light intensity, their photogenerated charge efficiencies increased in the order of PS-40 < PS-60 < PS-80, which is consistent with that of the increase in porosity (the increase in surface-to-volume ratio). It is demonstrated that the sensitivity to NO_2 is enhanced with UV irradiation, compared with that without irradiation, and the sensing characteristics of PS-80 are influenced by the largest amount under illumination. At the same time, the performances of the response and recovery to NO_2 of the porous silicon gas sensors are improved under UV irradiation.

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